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MEASURED MULTIMEDIA EMISSIONS FROM THE WOOD PRESERVING INDUSTRY

by

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FOREWORD

When energy and material resources are extracted, processed, converted, and used, the related pollutional impacts on our environment and even our health often require that new and increasingly more efficient pollution control methods be used. The Industrial Environmental Research Laboratory-Cincinnati (IERL-Ci) assists in developing and demonstrating new and improved methodologies that will meet these needs both efficiently and economically.

This report documents a recently completed project. Its purpose was to qualitatively and, when possible, quantitatively assess the organic emissions resulting from the evaporation and thermal destruction of wastewater generated by the wood preserving industry. The findings of this report can be used to determine the driving forces governing the loss of organic constituents to the atmosphere. The information contained in this report can also serve as a basis for future work. For further information, contact the Food and Wood Products Branch, IERL, Cincinnati, Ohio.

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ABSTRACT

Restriction of the discharge of wastewater generated during the preservation of wood has resulted in the increased use of evaporation techniques by the wood preserving industry. This report on the second phase of work described in EPA report 68-03-2584 discusses emissions that may occur to the atmosphere from thermal (pan) evaporation, spray pond evaporation, and direct thermal destruction of organic components in the wastewater. The information presented includes plant and evaporation device descriptions, test plans, sampling and analytical results, and conclusions and recommendations. Also presented are qualitative descriptions of the fugitive emissions that can occur during normal processing operations.

The primary conclusions are that organic compounds are emitted to the atmosphere during thermal (pan) evaporation. Organic emissions from the spray pond were below detectable levels. Fugitive organic emissions from the retort and vacuum vents were significant in concentration but of short duration. Thermal destruction of the compounds of interest may be a viable disposal option if the boiler is properly designed.

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LIST OF ABBREVIATIONS AND SYMBOLS

ABBREVIATIONS

SYMBOLS

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SECTION 1

INTRODUCTION

The wood preserving industry consists of approximately 475 production plants owned by approximately 300 companies. The primary products of this industry are utility poles, railroad ties, and construction materials, chemically treated to resist insect and fungi attack, improve weathering characteristics, and promote insolubility in water and fire retardance. The preservatives used to produce the desired product characteristics include creosote, a coal tar derivative; pentachlorophenol, a crystalline compound dissolved in light aromatic oil; and waterborne salts of arsenic, chromium, copper, zinc, and fluoride.

The application of the preservatives requires certain processing steps. The wood must first be debarked, formed (cut to size and shaped as necessary), and conditioned. The conditioning step removes the water from the wood, increasing its permeability and ability to accept the preservatives. Drying the wood can be done by air seasoning, tunnel drying, or kiln drying, all independent of the preserving step. The wood may also be conditioned in combination with the preserving step as in steam conditioning, boultonizing, or vapor drying. Each of these latter processes generates a wastewater stream containing wood extracts and preservatives which must be disposed of.

The toxic nature of the preservatives used by the wood industry has led the Effluent Guidelines Division of the Environmental Protection Agency (EPA) to promulgate regulations governing the disposal of the generated wastewater. The regulations presently in effect which do not allow the discharge of wastewater outside plant boundaries have led plant operators to develop treatment technologies other than direct discharge. The primary purpose of this report is to discuss the results of test programs conducted to quantify the uncontrolled transfer of toxic organic species contained in the wastewater to other medias.

The wastewater treatment or disposal technologies developed by the industry include plant modifications, improved oil/water separation, wastewater treatment, and evaporation. Evaporation includes thermal (pan) evaporation, cooling towers, spray ponds, and solar ponds. Under EPA contract 68-03-2584, an operating cooling tower was tested which showed virtually no discharge of organics. In addition, the thermal (pan) evaporation technique was evaluated in the laboratory; this work showed a significant fraction of the organic compounds in the wastewater being discharged to the atmosphere. To verify the release of organics from thermal (pan) evaporators, task 28 of EPA contract 68-03-2567 was funded. Also included in this task was the field testing of a spray evaporation pond and examination of wastewater disposal in an industrial steam boiler.

The scope of task 28 included plant identification, plant surveys, and site selections. The program objectives were to qualitatively and quantitatively evaluate multimedia emissions from a thermal (pan) evaporation device (including fugitive emissions from the treatment system), a spray pond system, and an industrial boiler using the oil-laden wastewater as supplemental fuel.

Section 2 of this report presents the conclusions reached during the execution of this task, followed by the recommendations in Section 3. Section 4 discusses the wastewater evaporation options available to plant operators, as well as thermal destruction of the wastewater. Sections 5 through 7 discuss the results of the thermal (pan) evaporation, the spray evaporation, and the boiler disposal test programs, respectively. Finally, Section 8 presents the fugitive emissions assessment.

Three appendices, one for each test program, presents all the details of the field sampling programs. Included in each appendix is the data collected in the field for that test program.

SECTION 2

CONCLUSIONS

The results of this program confirmed the discharge of organic compounds during wastewater evaporation in thermal (pan) evaporators and showed that the emissions were greater than usual predictive methods would indicate. Spray pond emissions were such that the cryogenic sampling systems used did not yield enough sample material to reach the sensitivity needed to detect the low volatility components of the wastewater. Therefore, of the evaporation systems studied, thermal (pan) evaporation is the least satisfactory and spray ponds the most satisfactory in terms of organic emissions.

The destruction of the organic compounds in an industrial steam boiler may be a viable disposal option if the boiler is designed properly. The system tested did not reach a 99.99 percent destruction efficiency, and certain dioxins and furans were present in the ash streams.

Industrywide, the air emissions from wastewater handling are on the order of 50 to 100 metric tons/year. Major fugitive emissions, although of high concentration, are of relatively short duration and low volume. Finally, though localized problems may occur, the industry as a whole is not a significant emitter of organics to the atmosphere. Table 2-1 presents a summary of the organic emissions discharged from the evaporation devices.

TABLE 2-1. SUMMARY TABLE

	Emissions concentration (ppm or μg/g)
Thermal evaporator	[illegible]
Spray pond evaporator	[illegible]
Retort emissions	[illegible]
Vacuum vent emissions	22,000 – 52,000

SECTION 3

RECOMMENDATIONS

If evaporation technology is to be employed, thermal (pan) evaporation is the greatest emitter of organic components to the atmosphere and its use should be minimized. Regardless of the evaporator used, care should be taken to develop oil/water separation techniques which minimize oil and sludge carryover to the evaporator. Further, a program should be conducted to establish the best available separation systems or to develop methods to enhance the operation of existing systems.

The destruction of wood preserving wastes in boilers is a viable disposal technology if the boiler is designed appropriately. It is recommended that a program be conducted to determine the proper injection (atomization) methods, and the residence times and temperatures necessary to completely destroy the organics in the waste. This incineration study also should be extended to the ash and sludge. Larger ash and sludge samples should be taken to obtain a better speciation and quantitation of the chlorinated dibenzo-p-dioxins and chlorinated dibenzofurans. In addition a careful evaluation should be conducted of the partitioning of these organic components between the bottom ash, mechanical hopper ash, and baghouse ash.

SECTION 4

WASTEWATER TREATMENT AND DISPOSAL BY EVAPORATION OR THERMAL DESTRUCTION

The treatment of wood with preservatives requires impregnation of the wood with toxic materials designed to protect it from attack by insects, fungi, weather, or fire. The processing steps include wood preparation (debarking, shaping, drying) and preservative application. The preservative can be applied using either pressure or nonpressure techniques. Nonpressure techniques are used when only minimal treatment is necessary. Pressure processes require the use of pressure or vacuum steps, either for preservative application or for combinations of wood conditioning (to increase permeability) and preservative application. Wood conditioning processes generate steam (due to the water content of the wood and the pressure/temperature/vacuum operations) which contains wood extractives and organic constituents from the preservative formulation. The heat content of the steam volatilizes low-molecular-weight organic compounds such as benzene and toluene, or atomizes drops of emulsified preservative, carrier oil, and water. When the resulting vapors are removed from the retort and condensed, the condensate contains water, free oils (and preservatives), emulsified oils (and preservatives), and wood extractives. Following removal of the free oils, the wastewater stream is transported to a disposal facility.

Industry's technical response to requirements for process wastewater control has included increased evaporation of water using thermal (pan) evaporators, spray and solar ponds, and cooling towers to decrease aqueous discharges. The principle behind the evaporation of the wastewater is to dispose of the water fraction while leaving the organic constituent for subsequent recycling to the process or landfill disposal. Since volatile and other low-molecular-weight organic constituents are present in the wastewater, they may be released to the atmosphere. This section describes each evaporation device and summarizes the emissions from it.

4.1 SURFACE EVAPORATION EMISSIONS

While evaporative processes allow plant operators to achieve zero wastewater discharge, they are operated under the assumption that no organic compounds are transferred to the air. Under EPA contract 68-03-2584, a program was conducted to determine if organic compounds were emitted to the atmosphere. The primary results of this program showed that organic components of the wastewater were discharged during evaporation.

The mathematical expression for the evaporation rate of chlorinated phenolic and other organic chemical pollutants from the surface of wastewater evaporation systems (thermal ponds or pan evaporators) can be developed from Fick's first law of diffusion. The following qualifying assumptions must be made:

- The system is at steady state (i.e., the liquid is at equilibrium with the gas at the liquid surface)
- The wastewater is an ideal solution
- There is a stagnant layer of air above the pond
- The vaporized organic compound forms an ideal gas mixture with air
- The solubility of air in the wastewater is negligible
- There is constant temperature and pressure in the stagnant air layer

With these assumptions, the minimum evaporation rate of each organic pollutant in the wastewater can be estimated using equation 1. This equation is expressed in terms of total and partial pressures:

$$N_A \bigg|_{z=z_1} = \frac{P_T D_{AB}/RT}{(z_2 - z_1)} \cdot \ln\left(\frac{P_T - P_{A_{Z2}}}{P_T - P_{A_{Z1}}}\right) \tag{1}$$

where:

N_A = molar flux of species A into B in the z direction, gmoles $L^{-2}t^{-1}$

P_T = total pressure, atm

D_{AB} = binary diffusivity for system composed of species A and B, L^2t^{-1}

P_{A_Z} = partial pressure of species A, atm

R = gas constant, 82.05 cm^3 atm $gmole^{-1}\,{}^oK^{-1}$

T = ambient air temperature, ^oK

z_2-z_1 = film thickness, cm

This expression shows the diffusivity and partial pressures impact on the rate of organic emissions: as temperature increases, the diffusivity increases. Therefore, higher-molecular-weight compounds can be driven out of solution.

In estimating the evaporation rate of organic vapors into air, it is assumed that the diffusion layer (z_2-z_1) is finite, that the air is stagnant and insoluble in the organic compound within that layer, and that the contained wastewater surface is quiescent. Therefore, if the air above the surface is turbulent, z_2-z_1 approaches zero, maximizing the transfer rate of the organics to the atmosphere.

The diffusivity and vapor pressures calculated from these equations can be used in estimating the evaporation rate of a pure organic liquid into air if the organic constituents formed a layer over the wastewater. To estimate the evaporation rate of an organic liquid from an aqueous solution (emulsion), it is assumed that the organic compound forms an ideal solution with water and that its vapor forms an ideal mixture in air. The evaporation rate of the organic from the solution is given by the product of the pure liquid evaporation rate and the mole fraction of organic in the wastewater.

It then was demonstrated in the laboratory that organic material is stripped from water solutions. The transfer of chlorinated organics from water solutions to the atmosphere is controlled by their rate of diffusion and concentration in water and the thermal driving force.

This evaporation model is applicable to solar ponds and thermal (pan) evaporators. A solar pond is a contained area where the wastewater is placed and allowed to evaporate. The pond may be lined or unlined. An unlined pond depends on soil attenuation to prevent organic materials from entering underlying aquifers. A lined pond is designed so that the evaporation rate exceeds the annual precipitation rate for a given geographical area. Solar ponds require large land usage, and federal regulations now require that ponds containing hazardous materials meet berm maintenance requirements and use monitoring wells for leachate control. These regulations may cause plant operators to install other evaporation technology.

The evaporation process can be accelerated by applying heat directly to evaporate the water, as in a thermal (pan) evaporator. In this system, the wastewater is contained in a vessel, such as a tank or lined pond, with an external heat source, such as boiler steam or the condenser system, to increase the solution temperature. The wastewater can be used as a cooling fluid to condense the vapor from the retort then recycle back to the evaporation system. Again, as the temperature is increased, an increase in organic emissions is predicted.

4.2 DROPLET EVAPORATION EMISSIONS

Another mechanism for enhancing evaporation is the formation of droplets. This method creates large liquid surface areas, promoting greater liquid/air contact and accelerated evaporation rates.

The evaporation rate of organic compounds from a droplet of wastewater can be estimated using an equation for the evaporation rate of a free-falling drop. Assuming that the evaporation rate is sufficiently small not to distort the velocity and concentration profiles, and that the mass transfer coefficient is independent of mass transfer rate, the resulting equation for predicting the evaporation rate is shown in equation 2:

$$W_a = \frac{\pi D C_f D_a}{4} \cdot \frac{x_{a_o} - x_{a_\infty}}{1 - x_{a_o}} \left[2.0 + 0.60 \left(\frac{D V_\infty \rho_f}{M_f} \right)^{1/2} \left(\frac{M}{\rho D} \right)_f^{1/3} \right] \qquad (2)$$

where:

W_a = evaporation rate, gmole/sec

D = droplet diameter, cm

C_f = molar concentration of air, 3.88×10^{-5} gmole/cc

D_a = diffusivity, cm^2/sec

X_a = vapor pressure of the liquid

V_∞ = velocity of droplet (assume terminal velocity), cm/sec

ρ_f = density of air, 1.12×10^{-3} g/cc

M_f = viscosity of air

This evaporation system again is impacted by diffusivity and partial pressure; air resistance also affects the rate of evaporation.

This evaporation model is applicable to spray pond systems and cooling towers. A spray pond is a contained area (lined or unlined pond) which has a pumping system connected to spray nozzles. This system decreases both the land required by a solar pond and the effect of negative climatic impacts.

The use of a cooling tower is only applicable to Boulton conditioning systems. As the water vapor from the retort is condensed, it gives up heat. The condensed wastewater is accumulated, then sent to the oil/water separator. The effluent wastewater from the oil/water separator is added to the cooling water that recirculates through the condenser and sent through the cooling tower: the waste heat promotes evaporation. In steaming plants, there is insufficient waste heat to evaporate the volume of wastewater generated.

A field test program was conducted at a site utilizing a cooling tower to measure the presence of organic compounds in the air stream. It was found that low-molecular-weight compounds were emitted to the atmosphere but that nonvolatile organics remained in solution.

Other evaporation processes are used by the wood preserving industry such as land irrigation. The wastewater is sprayed onto a field, during which droplet evaporation occurs, after which solar evaporation takes place and water percolates into the soil.

4.3 EMISSIONS SUMMARY

Each of the treatment processes discussed results in the formation of a sludge. The amount of solid waste material generated depends on the preservative used, and the effectiveness of the oil/water separator and the treatment technologies employed. This material is typically disposed in landfills (onsite, if land is available, or offsite). Incineration of solid waste is not now widely practiced.

Other sources of organic emissions, in addition to the evaporator discharge, include fugitive emissions such as the dense vapor plumes emitted as the pressure vessel is opened and wood charge removed, and emissions from the treated wood as it cools and the vacuum exhaust. Quantifying data describing the emissions were not identified in the literature. A primary purpose of this program was to collect additional field data to further evaluate the multimedia emissions and disposal options available to the wood preserving industry.

SECTION 5

CHARACTERIZATION OF MULTIMEDIA EMISSIONS FROM A THERMAL (PAN) EVAPORATION DEVICE

A field test program was conducted at a wood preserving plant using thermal (pan) evaporation to reduce its generated wastewater volume. The program was designed to determine the organic emissions from two thermal (pan) evaporators, one evaporating wastewater containing penta and other chlorinated phenolic compounds, and one evaporating wastewater containing creosote components (polynuclear aromatic hydrocarbons (PAH's)). Each stream was qualitatively and semiquantitatively analyzed for organic compounds, including chlorinated phenols, chlorinated dibenzo-p-dioxins, chlorinated dibenzofurans, and PAH's.

5.1 PROGRAM DESCRIPTION AND RESULTS

This program focused on those primary multimedia effluents generated by the plant that were expected to have the greatest environmental impact in terms of gaseous and solid discharges. The sampling points of interest were the ducted air emissions and solid wastes from wastewater treatment. Material balance estimates were conducted around each evaporator. A primary objective of this program was to quantitate the emission rate of organic compounds from the evaporation devices.

5.1.1 Test Site

The wood treating facility selected for field testing employed two treating cylinders using the Boulton conditioning process. One cylinder could treat wood with penta formulations, while the other cylinder could treat wood with either penta or creosote.

Condensate generated from the individual treating processes was handled by discrete subsurface oil/water separators on a batch basis. The recovered oil fraction was returned to bulk storage tanks for reuse in the process. Separated sludges and wastewater were routed to the appropriate thermal (pan) evaporators -- one penta and one creosote -- for volume reduction. Figure 5-1 presents a schematic of the plant wastewater/preservative recovery system.

Each evaporator was operated on a semibatch basis. As the wastewaters were transferred to their respective evaporators, steam from the boilers was pumped through steam coils in the tanks to heat the wastewaters to boiling, driving off the water. This process was continued until an oil/preservative layer accumulated which was returned to the preservative work tanks. Semiannually the evaporators were opened, and the nonpumpable sludge layer removed and shipped offsite to a landfill.

5.1.2 Field Test Program

The sampling program conducted included each of these tests:

- Source emission sampling at the penta and creosote thermal (pan) evaporator outlets
- Total hydrocarbon determinations at each air emission point
- Specific low-molecular-weight hydrocarbon determinations at each emission point
- Grab samples of:
  - -- Penta thermal (pan) evaporator contents
  - -- Creosote thermal (pan) evaporator contents
  - -- Bulk penta in treating oil

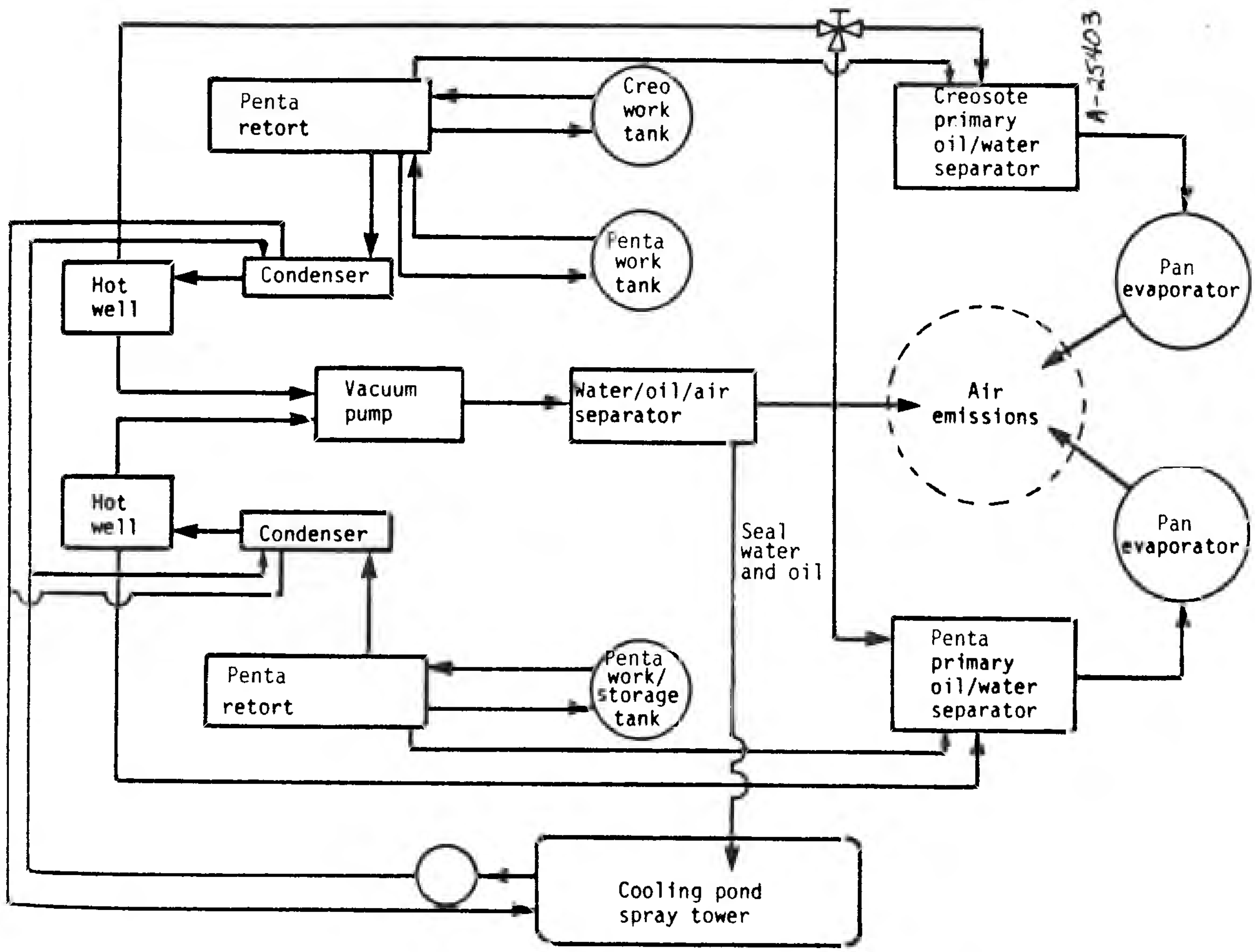

Figure 5-1. Schematic of wood preserving plant wastewater/preservative recovery system.

-- Bulk creosote

-- Penta oil/water separator (both fractions)

— Creosote oil/water separator (both fractions)

The sample collection matrix is shown in table 5-1. Source emissions sampling was conducted using the EPA Method 5 sampling train with XAD-2 resins for nonvolatile organic compounds. Volatile organic emissions were measured using field gas chromatography (GC) techniques. Samples of the liquid fractions were randomly collected by grab sampling during each test series. A complete discussion of the field testing and the test data are contained in appendix A.

5.1.3 Data Presentation for Pan Evaporation

The concentration data for the pan evaporator tests are given in tables 5-2 to 5-7. Average values for the penta pan evaporator tests and the creosote pan evaporator tests are shown in tables 5-8 and 5-9, respectively. Note that in test 4 on the penta evaporator, the units of emission are in g/sm^3, rather than mg/sm^3 for all other tests.

Concentrations of evaporator gaseous emissions are calculated by dividing the total milligrams of the component collected in the organic resins by the water volume collected in the impinger train; the water volume data are corrected to standard gas volume. For example, during test 4 on the penta evaporator, 24,000 mg (24g) of penta was collected. The condensed water volume collected was 598 ml. This translates to 1.76 m^3 of water vapor at 23^oC and 1 atm, as follows:

$$598g\ H_2O\ell \times \frac{1\ \text{mole}}{18g} \times \frac{22.414\ \text{liters}}{\text{mole}\ (0^oC,\ 1\ \text{atm})} \times \frac{296^oK}{273^oK} \times \frac{10^{-3}m^3}{\text{liter}} \quad (1)$$

TABLE 5-1. SUMMARY OF COLLECTED SAMPLES

Sample location number	1	2	3	4
Collection method / Location description	Penta oil/ water retort	Creosote oil/ water separator	Penta evaporator	Creosote evaporator
Day 1 (Setup)				
Day 2				
XAD-2			X	X
Field GC			X	X
Liquid grab sample	X (2)	X (2)	X (2)	X (2)
Solid grab sample			X	X
Day 3				
XAD-2			X	X
Field GC			X	X
Liquid grab sample	X (2)	X (2)	X (2)	X (2)
Solid grab sample			X	X
Day 4				
XAD-2			X	X
Field GC			X	X
Liquid grab sample	X (2)	X (2)	X (2)	X (2)
Solid grab sample			X	X
Day 5 (Cleanup)				

TABLE 5-2. PENTA PAN EVAPORATOR — TEST 2

Stream	Working solution	Oil/water recycle	Waste-water	Pan water	Pan sludge	Pan vent
Date	9/23	9/24	9/24	9/24	9/23	9/24
Time	—	1300	1245	0900	--	1200
Concentration*						
Penta	44,000	40,000	14,000	140	6.2	1.8
Phenol	<200	<10	<10	0.5	1.2	<0.5
Fluoranthene	430	3,800	970	7.9	2.0	1.0
Naphthalene	3,800	3,700	1,500	0.4	1.1	2.0
Benzo(a)anthracene	<100	540	200	3.7	0.5	0.11
Benzo(a)pyrene	<100	110	40	0.1	0.05	<0.1
Benzofluoranthenes	<100	380	110	0.1	0.2	<0.1
Chrysene	<100	520	180	3.7	0.4	0.10
Acenaphthylene	170	140	310	0.1	0.05	<0.1
Anthracene	230	400	180	1.2	0.5	0.17
Benzo(g,h,i)perylene	<200	30	<10	<0.1	0.1	<0.1
Fluorene	1,100	2,700	850	1.4	1.0	<0.1
Phenanthrene	1,700	5,000	1,800	9.5	3.5	1.0
Dibenzo(a,h) anthracene	<200	4	<10	<0.1	0.1	<0.5
Indeno(1,2,3-c,d) pyrene	<200	15	<10	<0.1	0.1	<0.5
Pyrene	350	3,500	710	6.1	1.4	0.8
Benzene	<1	0.3	<10	<0.1	0.2	NA
Toluene	18	27	<10	<0.1	0.3	NA
Ethylbenzene	23	19	<10	<0.1	0.2	NA

*Concentration units are µg/g (ppm w/w) for solids, µg/ml (ppm w/w) for liquids, and mg/sm^3 (at 23°C, 1 atm) for gases

TABLE 5-3. PENTA PAN EVAPORATOR — TEST 3

Stream	Working solution	Oil/water recycle	Waste-water	Pan water	Pan sludge	Pan vent
Date	9/23	9/25	9/25	9/25	9/23	9/25
Time	—	1500	1510	--	--	0800
Concentration*						
Penta	44,000	45,000	980	70	6.2	3.4
Phenol	<200	<10	<10	0.4	1.2	0.65
Fluoranthene	430	2,800	2,000	2.7	2.0	5.2
Naphthalene	3,800	2,000	220	0.1	1.1	3.0
Benzo(a)anthracene	<100	430	290	1.4	0.5	0.29
Benzo(a)pyrene	<100	96	68	<0.1	0.05	<0.1
Benzofluoranthenes	<100	320	190	<0.1	0.2	<0.1
Chrysene	<100	400	420	1.0	0.4	0.26
Acenaphthylene	170	370	1,600	0.3	0.05	1.3
Anthracene	230	1,100	400	0.4	0.5	2.3
Benzo(g,h,i)perylene	<200	7	<20	<0.1	<0.1	<0.1
Fluorene	1,100	2,400	2,100	2.6	1.0	3.1
Phenanthrene	1,700	4,000	3,600	2.4	3.5	9.2
Dibenzo(a,h)anthracene	<200	<10	<20	<0.1	<0.1	<0.1
Indeno(1,2,3-c,d)pyrene	<200	28	<20	<0.1	<0.1	<0.1
Pyrene	350	1,900	1,300	2.0	1.4	3.2
Benzene	<1	1.2	0.2	<0.2	<0.2	
Toluene	18	77	0.1	<0.2	0.3	
Ethylbenzene	23	2.3	1.2	<0.2	<0.2	

*Concentration units are µg/g (ppm w/w) for solids, µg/ml (ppm w/w) for liquids, and mg/sm^3 (at 23°C, 1 atm) for gases

TABLE 5-4. PENTA PAN EVAPORATOR — TEST 4

Stream	Working solution	Oil/water recycle	Waste-water	Pan water	Pan sludge	Pan vent
Date	9/23	9/25	9/25	9/26	9/23	9/26
Time	—	1500	1510	--	--	1135
Concentration*						
Penta	44,000	45,000	980	41	6.2	30
Phenol	<200	<10	<10	0.3	1.2	0.52
Fluoranthene	430	2,800	2,000	1.2	2.0	1.7
Naphthalene	3,800	2,000	220	0.3	1.1	5.8
Benzo(a)anthracene	<100	430	290	0.9	0.5	0.20
Benzo(a)pyrene	<100	96	68	<0.1	0.05	<5x10-
Benzofluoranthenes	<100	320	190	<0.1	0.2	0.043
Chrysene	<100	400	420	0.7	0.4	0.190
Acenaphthylene	170	370	1,600	0.1	0.05	1.370
Anthracene	230	1,100	400	0.2	0.5	0.740
Benzo(g,h,i)perylene	<200	7	<20	<0.1	<0.1	<5x10-
Fluorene	1,100	2,400	2,100	1.7	1.0	1.7
Phenanthrene	1,700	4,000	3,600	1.5	3.5	1.5
Dibenzo(a,h)anthracene	<200	<10	<20	<0.1	<0.1	<5x10-
Indeno(1,2,3-c,d)pyrene	<200	28	<20	<0.1	<0.1	<5x10-
Pyrene	350	1,900	1,300	0.9	1.4	1.4
Benzene	<1	1.2	0.2	<0.2	<0.2	
Toluene	18	77	0.1	0.2	0.3	
Ethylbenzene	23	2.3	1.2	0.2	<0.2	

*Concentration units are μg/g (ppm w/w) for solids, μg/ml (ppm w/w) for liquids, and mg/sm^3 (at 23^{o}C, 1 atm) for gases

TABLE 5-5. CREOSOTE PAN EVAPORATOR — TEST 2

Stream	Working solution	Oil/water recycle	Waste-water	Pan water	Pan sludge	Pan vent
Date	9/23	9/24	9/24	9/24	9/23	9/24
Time	—	—	—	0830	—	1450
Concentration*						
Penta	17,000	3,600	12	3.4	26.0	<0.15
Phenol	400	1,500	7	11	30	15
Fluoranthene	32,000	33,000	20	20	590	25
Naphthalene	24,000	33,000	42	13	680	200
Benzo(a)anthracene	20,000	23,000	10	14	390	0.4
Benzo(a)pyrene	600	610	2	24	91	<0.05
Benzofluoranthenes	650	530	4	5.7	190	0.05
Chrysene	15,000	19,000	10	8.9	240	0.3
Acenaphthylene	5,700	3,400	2	1.2	840	7
Anthracene	12,000	69,000	7	9.9	260	32
Benzo(g,h,i)perylene	<500	<500	0.2	0.6	10	<0.05
Fluorene	36,000	38,000	16	2.5	660	110
Phenanthrene	37,000	41,000	19	3.2	1100	98
Dibenzo(a,h)anthracene	<500	<500	0.2	0.9	<10	<0.05
Indeno(1,2,3-c,d)pyrene	<500	<500	0.3	0.7	16	<0.05
Pyrene	27,000	27,000	15	16	440	16
Benzene	26	<50	<0.1	<0.1	6.7	
Toluene	2.7	<50	<0.1	<0.1	1.4	
Ethylbenzene	<0.5	<50	<0.1	<0.1	0.3	

*Concentration units are μg/g (ppm w/w) for solids, μg/ml (ppm w/w) for liquids, and mg/sm^3 (at 23^{o}C, 1 atm) for gases

TABLE 5-6. CREOSOTE PAN EVAPORATOR — TEST 3

Stream	Working solution	Oil/water recycle	Waste-water	Pan water	Pan sludge	Pan vent
Date	9/23	9/25	9/25	9/25	9/23	9/25
Time	—	—	—	—	—	1005
Concentration*						
Penta	17,000	1,300	8.3	7.6	26.0	2.7
Phenol	400	800	5.2	31	30	58
Fluoranthene	32,000	13,000	140	9.3	590	20
Naphthalene	24,000	38,000	200	10	680	2.7x10
Benzo(a)anthracene	20,000	9,200	60	4.5	390	1.4
Benzo(a)pyrene	600	3,000	6.1	0.6	91	0.2
Benzofluoranthenes	650	500	15	1.4	190	0.7
Chrysene	15,000	5,400	50	3.7	240	1.2
Acenaphthylene	5,700	5,700	6	0.3	840	29
Anthracene	12,000	8,000	56	2.8	260	68
Benzo(g,h,i)perylene	<500	730	<10	<0.1	10	<0.05
Fluorene	36,000	35,000	110	8.9	660	550
Phenanthrene	37,000	22,000	190	15	1100	200
Dibenzo(a,h)anthracene	<500	1,500	<10	<0.1	<10	<0.05
Indeno(1,2,3-c,d)pyrene	<500	1,300	<10	0.1	16	<0.05
Pyrene	27,000	10,000	100	6.7	440	13
Benzene	26	27	<0.1	<0.1	6.7	
Toluene	2.7	0.5	<0.1	<0.1	1.4	
Ethylbenzene	<0.5	6.8	<0.1	<0.1	0.3	

*Concentration units are μg/g (ppm w/w) for solids, μg/ml (ppm w/w) for liquids, and mg/sm^3 (at 23°C, 1 atm) for gases

TABLE 5-7. CREOSOTE PAN EVAPORATOR — TEST 4

Stream	Working solution	Oil/water recycle	Waste-water	Pan water	Pan sludge	Pan vent
Date	9/23	9/25	9/25	9/25	9/23	9/25
Time	—	—	—	—	—	1300
Concentration*						
Penta	17,000	1,300	8.3	0.5	26.0	1.6
Phenol	400	800	5.2	35	30	<0.05
Fluoranthene	32,000	13,000	140	6.0	590	21
Naphthalene	24,000	38,000	200	6 4	680	2.2×10^3
Benzo(a)anthracene	20,000	9,200	60	2.4	390	1.2
Benzo(a)pyrene	600	3,000	6.1	0.4	91	0.3
Benzofluoranthenes	650	500	15	0.8	190	1.3
Chrysene	15,000	5,400	50	1.9	240	0.9
Acenaphthylene	5,700	5,700	6	0.2	840	44
Anthracene	12,000	8,000	56	1.4	260	44
Benzo(g,h,i)perylene	<500	730	<10	<0.1	10	<0.05
Fluorene	36,000	35,000	110	6.0	660	580
Phenanthrene	37,000	22,000	190	12	1100	260
Dibenzo(a,h)anthracene	<500	1,500	<10	<0.1	<10	<0.05
Indeno(1,2,3-c,d)pyrene	<500	1,300	<10	<0.1	16	<0.05
Pyrene	27,000	10,000	100	4.2	440	16
Benzene	26	27	<0.1	3.4	6.7	
Toluene	2.7	0.5	<0.1	<0.2	1.4	
Ethylbenzene	<0.5	6.8	<0.1	0.3	0.3	

*Concentration units are μg/g (ppm w/w) for solids, μg/ml (ppm w/w) for liquids, and mg/sm^3 (at 23°C, 1 atm) for gases

TABLE 5-8. PENTA PAN EVAPORATOR — AVERAGE VALUES

Stream	Working solution	Oil/water recycle	Waste-water	Pan water	Pan sludge	Pan vent
Volume*			3,400	8×10^4	109	6×10^3
Concentration**						
Penta	44,000	42,000	7,000	80	6.2	10^4
Phenol	<200	<10	<10	0.6	1.2	200
Fluoranthene	430	3,300	1,500	4.3	2.0	600
Naphthalene	3,800	2,800	850	0.2	1.1	2×10^3
Benzo(a)anthracene	<100	480	250	1.9	0.5	70
Benzo(a)pyrene	<100	100	60	<0.1	0.05	<5
Benzofluoranthenes	<100	350	150	<0.1	0.2	10
Chrysene	<100	460	300	1.7	0.4	60
Acenaphthylene	170	260	950	0.2	0.05	100
Anthracene	230	750	290	0.6	0.5	300
Benzo(g,h,i)perylene	<200	18	<10	<0.1	0.1	<5
Fluorene	1,100	2,600	1,500	1.5	1.0	600
Phenanthrene	1,700	4,500	2,700	4.0	3.5	500
Dibenzo(a,h)anthracene	<200	4	<10	<0.1	0.1	<5
Indeno(1,2,3-c,d)pyrene	<200	22	<10	<0.1	0.1	<5
Pyrene	350	2,700	1,000	3.2	1.4	500
Benzene	<1	6	<10	<0.2	<0.2	<5
Toluene	18	54	<10	<0.2	0.3	<5
Ethylbenzene	23	10	<10	<0.2	<0.2	<5

*Solid and liquid flowrates are averages based on monthly production figures (kg/day or l/day). Gas volumes are based on average daily decreases in tank volume (sm^3/day).

**Concentration units are µg/g (ppm w/w) for solids, µg/ml (ppm w/w) for liquids, and mg/sm^3 (at 23°C, 1 atm) for gases

TABLE 5-9. CREOSOTE PAN EVAPORATOR — AVERAGE VALUES

Stream	Working solution	Oil/water recycle	Waste-water	Pan water	Pan sludge	Pan vent
Volume*	—	—	5200 l/day	40000 l	114 kg/day	7300 sm^3/day
Concentration**						
Penta	17,000	2,500	10	6.2	26.0	2
Phenol	400	1,100	6	23	30	30
Fluoranthene	32,000	23,000	80	25	590	23
Naphthalene	24,000	36,000	120	12	680	2.5×10^3
Benzo(a)anthracene	20,000	16,000	35	16	390	1
Benzo(a)pyrene	600	1,800	4	6.7	91	<0.2
Benzofluoranthenes	650	520	10	3	190	0.6
Chrysene	15,000	12,000	30	10	240	0.8
Acenaphthylene	5,700	4,600	4	1.4	840	30
Anthracene	12,000	39,000	30	10	260	50
Benzo(g,h,i)perylene	<500	600	<5	<0.1	10	<0.05
Fluorene	36,000	37,000	63	27	660	400
Phenanthrene	37,000	32,000	110	34	1100	190
Dibenzo(a,h)anthracene	<500	1,000	<5	0.2	<10	<0.05
Indeno(1,2,3-c,d)pyrene	<500	900	<5	<0.2	16	<0.05
Pyrene	27,000	18,000	55	19	440	15
Benzene	26	<40	<0.1	<0.1	6.7	
Toluene	2.7	<25	<0.1	<0.1	1.4	
Ethylbenzene	<0.5	<25	<0.1	<0.1	0.3	

*Solid and liquid flowrates are averages based on monthly production figures (kg/day or l/day). Gas volumes are based on average daily decreases in tank volume (sm^3/day).

**Concentration units are μg/g (ppm w/w) for solids, μg/ml (ppm w/w) for liquids, and mg/sm^3 (at 23°C, 1 atm) for gases

Thus, the average concentration of penta leaving the evaporator during the test was:

$$\frac{24 \times 10^3 \text{ mg}}{0.807 \text{ sm}^3} \sim 3 \times 10^4 \text{ mg/sm}^3 \qquad (2)$$

System flowrates are based on plant operating information and field measurements. Between November 19 and December 31, 1980, the test plant generated 25,000 gal of wastewater from the creosote process and 16,000 gal from the penta process. The plant was on a 3-day/week treatment schedule for 18 days. The generation rates are calculated at approximately 5,200 l/day (1,400 gal/day) for the creosote process and 3,400 l/day (890 gal/day) for the penta process.

Between September 10 and November 18, 1980, 41,000 gal of water were evaporated in the penta pan evaporator, and 20 barrels (approximately 550 lb each) of sludge were recovered for disposal. Thus, approximately 32g sludge/liter of wastewater (0.27 lb/gal) were generated. For the creosote pan evaporator, the corresponding numbers are 73,000 gal, 24 barrels, and 22 g/l (0.15 lb/gal). From this, the rate of sludge generation is calculated to be 114 and 109 kg/day for the creosote and penta pan evaporators, respectively.

The driving force for vent emissions from the evaporator is boiling water. Volume emission rates based on pure water vapor are calculated from the rate volume change in the evaporators.

Given the diameter of the creosote evaporator (11 ft) and the average rate of change in the liquid height (0.997 inch/hr), the volume of water evaporated is estimated to be 5,370 l/day (1,420 gal/day), in agreement with the input rate. The corresponding numbers for the penta evaporator are 12-ft diameter, 0.698 inch/hr, and 4,470 l/day (1,180 gal/day) with approximate agreement. The liquid volumes are converted into the following gas volumes:

- 7.3×10^3 sm^3/day from the creosote evaporator
- 6×10^3 sm^3/day from the penta evaporator

A summary of sampling times and volumes is given in table 5-10. A schematic of the process, showing sample locations, is presented in figure 5-2.

5.1.4 Material Balances Around Evaporators

Material balance calculations made around each evaporator are shown in tables 5-11 and 5-12. Volume flowrates are the average daily rates calculated in the previous section. Values for the bulk streams are in kg/hr, including water from the vents; values for individual components are in g/hr.

The air emissions rate is predicted for each component by subtracting the output rate in the sludge from the input rate in the wastewater. The high vent rate uses the highest concentration of the component observed during testing, while the low value is from the lowest concentration observed. Both cases use the average volume rate of water boiled off. The average emission rate is the average of the high and low rates, not the rate calculated from the average vent concentration.

The average emission rate cannot be used for estimating emissions. As will be shown, a true average emission rate must be time weighted. Because the amount of time during the evaporation cycle that each component is emitted at a high concentration is not known, the time-weighted average is not available. A study of the tables, however, shows that the predicted emission rate falls between the high and low observed rates, making a fair estimate of the average hourly emissions. Table 5-13 shows the percent of input emitted to the atmosphere based on this average hourly rate: over 80 percent of almost every component (and 100 percent of some) are transferred to the air.

TABLE 5-10. SAMPLING DATA

Location/ run number		Date	Start time	Stop time	Sample time	Water volume* (ml)	Water volume** (sm^3)
Penta	2	9/24/80	1208	1238	30	1301.6	1.758
	3	9/25/80	0806	0825.5	19.5	972.5	1.314
	4	9/26/80	1135	1150	15	598.0	0.806
Creosote	2	9/24/80	1451	1547	56	1130.4	1.524
	3	9/25/80	1005	1050	45	762.3	1.028
	4	9/25/80	1302	1313.5	11.5	945.6	1.275

*Liquid

**Gas at 23°C and 1 atm (73°F and 760 mm Hg)

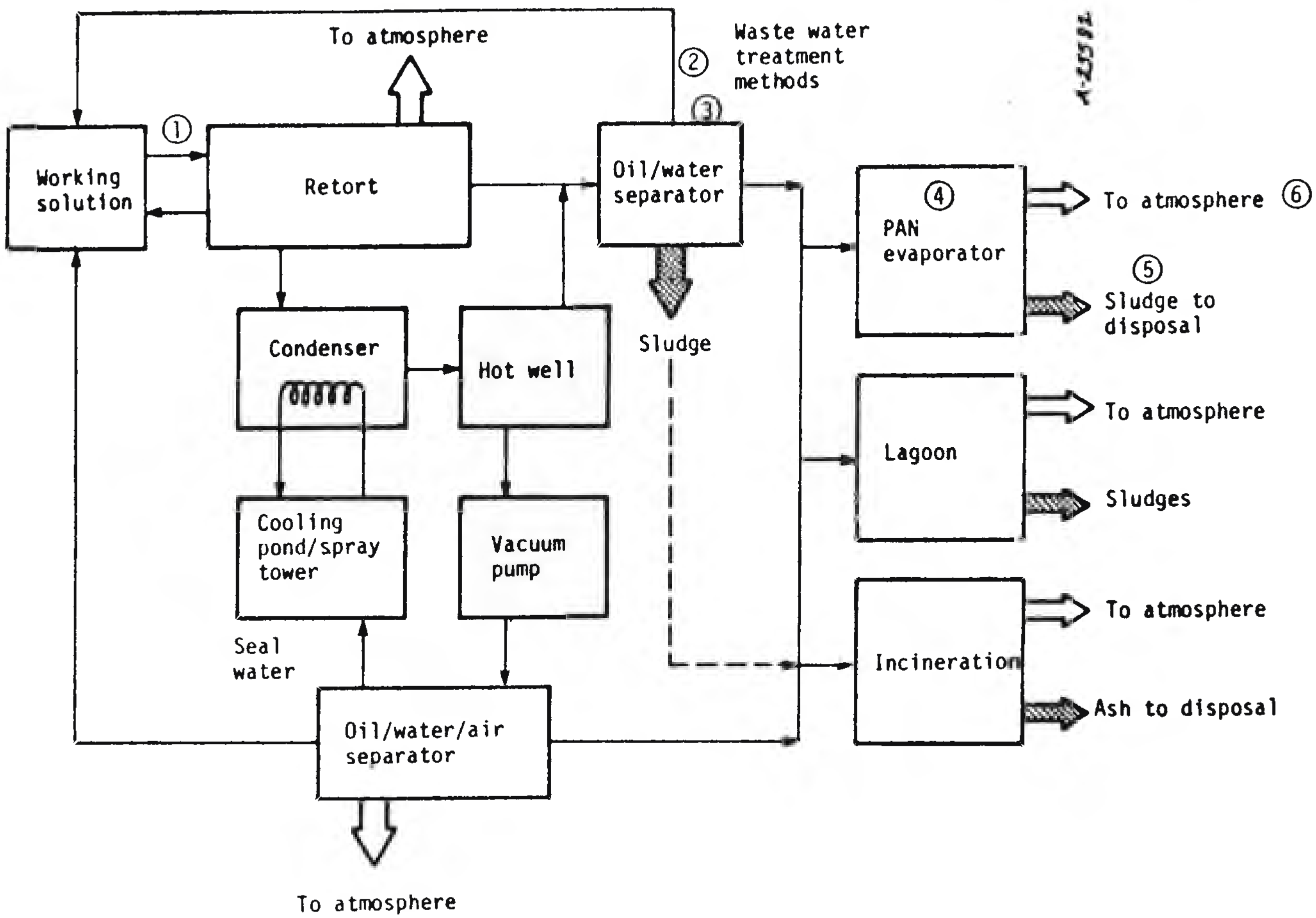

Figure 5-2. Sampling locations for thermal (pan) evaporator tests and fugitive emissions tests.

TABLE 5-11. CREOSOTE PAN EVAPORATOR -- MATERIAL BALANCE

Stream name	Wastewater in (g/hr)	Sludge out (g/hr)	Pred pan vent out (g/hr)	Obs high pan vent out (g/hr)	Obs low pan vent out (g/hr)	Obs av pan vent out (g/hr)
Stream (x 10^{-3})	217	4.8	212	—	—	223
Penta	2.2	0.12	2.1	0.812	0.045	0.43
Phenol	6.5	0.14	6.4	17	0.015	8.7
Fluoranthene	17.0	0.01	17	7.5	6.0	6
Naphthalene	26.0	3.3	23	810	60	430
Benzo(a)anthracene	7.60	1.9	5.7	0.35	0.12	0.27
Benzo(a)pyrene	0.87	0.44	0.43	0.09	0.015	0.05
Benzofluoranthenes	2.2	0.91	1.3	0.39	0.05	0.20
Chrysene	6.5	1.2	5.4	0.36	0.090	0.23
Acenaphthylene	0.87	4.03	-3.2	13	2.2	7.7
Anthracene	6.5	1.3	5.3	17	9.6	15
Benzo(g,h,i)perylene	1.09	0.05	1.04	0.015	0.015	0.01
Fluorene	13	3.2	10.5	150	33	104
Phenanthrene	24	5.3	19	65	29.5	50
Dibenzo(a,h)anthracene	1.09	0.002	1.09	<0.015	<0.015	<0.01
Indeno(1,2,3-e,d)pyrene	1.09	0.002	1.09	<0.015	<0.015	<0.01
Pyrene	12	2.1	9.8	4.8	3.9	4.4
Benzene	<0.022	0.032	<0.02	—	—	—
Toluene	<0.022	0.0067	<0.02	—	—	—
Ethyl benzene	<0.022	0.0014	<0.02	—	—	—

Obs a pan vent out (g/hr
223
0.43
8.7
6
430
0.27
0.05
0.20
0.23
7.7
15
0.01
104
50
<0.01
<0.01
4.4
--
--
--

TABLE 5-12. PENTA PAN EVAPORATOR -- MATERIAL BALANCE

Stream name	Wastewater in (g/hr)	Sludge out (g/hr)	Pred pan vent out (g/hr)	Obs high pan vent out (g/hr)	Obs low pan vent out (g/hr)	Obs av pan vent out (g/hr)
Stream (x 10^{-3})	142	4.5	138	—	--	186
Penta	994	0.03	994	7.5×10^{3}	0.42	3×10^{3}
Phenol	1.4	0.0005	1.4	160	ND	80
Fluoranthene	2.3	0.01	207	420	0.25	210
Naphthalene	121	0.005	121	1.5×10^{3}	0.50	750
Benzo(a)anthracene	36	0.0023	36	50	0.07	25
Benzo(a)pyrene	8.5	0.0002	8.3	ND	ND	ND
Benzofluoranthenes	21	0.0009	21	10	ND	5
Chrysene	43	0.0023	41	50	0.07	25
Acenaphthylene	135	0.0002	131	340	ND	170
Anthracene	41	0.0023	40	190	0.04	95
Benzo(g,h,i)perylene	<1.4	0.0005	<1.4	ND	ND	ND
Fluorene	213.0	0.0045	213.0	430	ND	220
Phenanthrene	383	0.0016	383	380	0.25	190
Dibenzo(a,h)anthracene	<1.4	0.00045	<1.4	ND	ND	ND
Indeno(1,2,3-e,d)pyrene	<1.4	0.00045	<1.4	ND	ND	ND
Pyrene	50	0.0063	50	350	0.2	180
Benzene	<1.4	0.0009	<1.4	ND	ND	ND
Toluene	<1.4	0.00004	<1.4	ND	ND	ND
Ethyl benzene	<1.4	0.0009	<1.4	ND	ND	ND

TABLE 5-13. PERCENT OF ORGANIC SPECIE EMITTED IN VENT

Specie	Creosote evaporator	Penta evaporator
Penta	95	100
Phenol	98	100
Fluoranthene	100	97
Naphthalene	88	100
Benzo(a)anthracene	75	100
Benzo(a)pyrene	50	98
Benzofluoranthene	60	100
Chrysene	80	95
Acenaphthylene	—	97
Anthracene	80	98
Benzo(g,h,i)perylene	100	—
Fluorene	80	100
Phenanthrene	79	100
Dibenzo(a,h)anthracene	100	—
Indeno(1,2,3-e,d)pyrene	100	—
Pyrene	80	100
Benzene	—	—
Toluene	—	—
Ethyl benzene	—	—

5.2 MODELS FOR THERMAL EVAPORATION

The original predictions for negligible organic emissions to the atmosphere from thermal (pan) evaporation were based on ideal solution vapor pressures (Raoult's law), and classical diffusion and mass transport theory. Previous laboratory work indicated that these predictions might be wrong (1) by postulating a hypothetical model applying regular solution theory and activity coefficients. This model could increase the emission rates several orders of magnitude, enough for measurement. The reported field tests verified that organic emissions do occur at a significant level.

Although study of the field data reveals a wide variation in the observed concentrations of organics in the emissions, these concentrations were well above predicted levels. Because the sampling times varied with respect to the evaporation cycle and the filling process was not continuous, a closer inspection of the process produced a new model for predicting emissions.

5.2.1 Model Description

Thermal evaporation is similar to laboratory batch steam distillation: wastewater is transferred to the evaporator, internal heating is applied by steam coils, and after a given period of time, more wastewater is put into the evaporator. As organics are driven out, their concentration in the system decreases. When the concentration of a specie falls to zero in most of the water, it falls to zero in the emission. Therefore, the concentration of the emitted specie is cyclic: the average concentration measured during a given test depends on when in the evaporation cycle the sample was taken.

Four physical regimes for evaporation have been identified:

- Static evaporation (ideal or regular solution)
- Steam distillation

- Controlled mass transfer evaporation from an infinite sink
- Flash evaporation

A qualitative description of the model follows with a brief mathematical description and sample calculations for each mechanism. Observed values are then compared to predicted values for each mechanism involving one compound.

Qualitative Description--

Thermal evaporation of organic components from a wastewater matrix can be modeled as a series of physical processes. Each mechanism depends on the phase distribution of the component under study. At the beginning of the cycle, the component is distributed among sludge, water, and oil. Steam distillation depletes the component in the (partially miscible) oil phase. The infinite source mass transfer mechanism then operates until the component can no longer be stripped significantly from the sludge. Finally, the static evaporation mechanism operates until the component has been stripped from the water or a new cycle begins. A diagram of the process is shown in figure 5-3. An expected gas phase concentration plot is given in figure 5-4.

A summary of the model follows:

- When water and component A exist as two partially immiscible liquids, steam distillation of component A occurs
- When the sludge can act as an infinite source of component A, the mass transfer rate from sludge to liquid to gas determines its concentration in the gas phase
- When component A is present solely in solution, static evaporation determines its approximate concentration in the gas phase

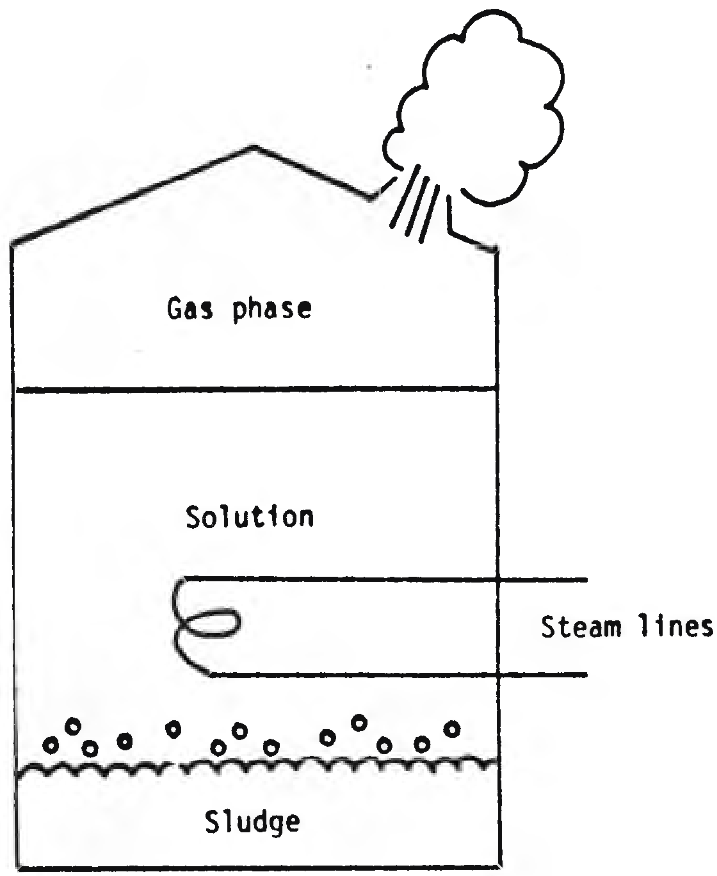

Figure 5-3. Thermal evaporation system.

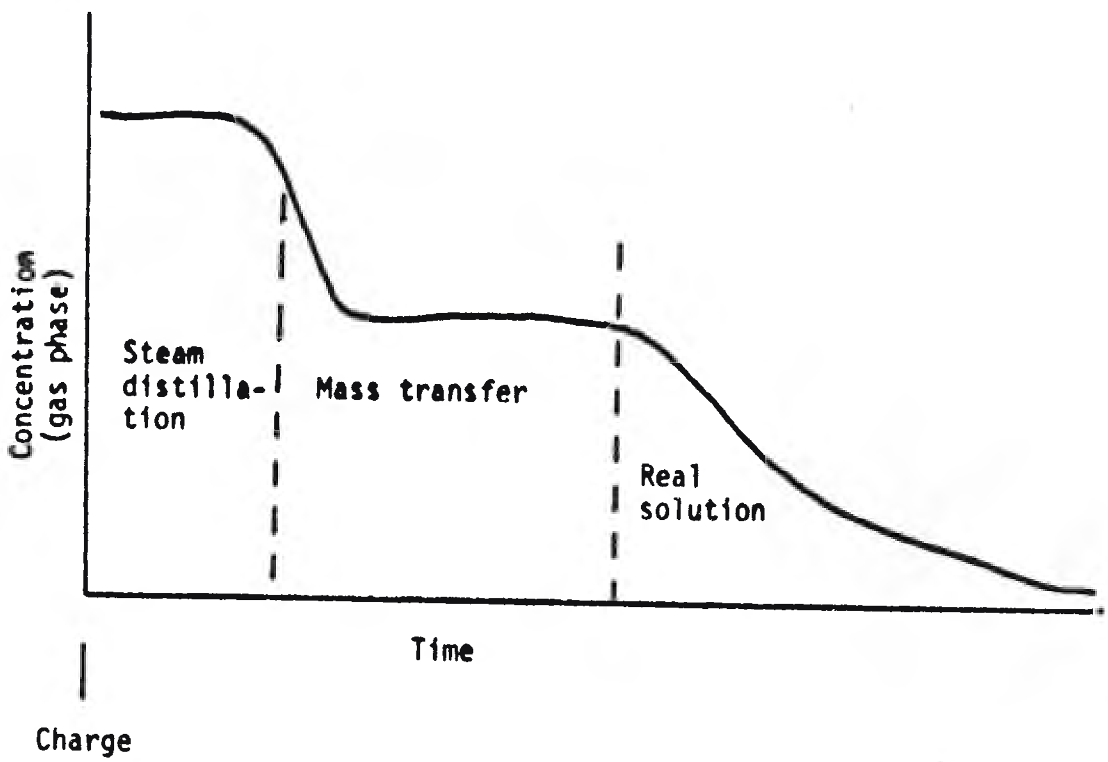

Figure 5-4. Thermal evaporation cycle.

- Flash evapoaration occurs only when the heat source is uncovered and well above the boiling point of the wastewater
- The duration of each mode differs for different components

Steam Distillation—

Immediately after charging, component A may exist as a partially miscible oil. If it does, its concentration in the gas phase is approximated by the pure steam distillation formula (2):

$$\frac{W_A}{W_{H_2O}} = \frac{M_A \, P_A^o}{M_{H_2O} \, P_{H_2O}^o} \tag{3}$$

where W_A = weight of component A in vapor phase

W_{H_2O} = weight of water in vapor phase

M_A = molecular weight of component A

M_{H_2O} = molecular weight of water

P_A^o = partial pressure of pure A at boiling temperature of mixture

$P_{H_2O}^o$ = partial pressure of water at boiling temperature

Calculations for various components and tests in tables 5-14 and 5-15 show some compounds very near steam distillation concentrations and some very far away. The lower the solubility and the higher the concentration (in the incoming wastewater), the closer the component comes to steam distillation concentration. The test time is also critical as shown by the differences between the penta pan evaporator tests 3 and 4. Test 3 was conducted just prior to the start of a new cycle, while test 4 was begun shortly after a new wastewater charge was placed in the evaporator.

TABLE 5-14. PENTA PAN EVAPORATION -- STEAM DISTILLATION MODEL

		Test 3		Test 4	
	$\frac{W_A}{W_B}$ PRED	$\frac{W_A}{W_B}$ OBS	$\frac{OBS}{PRED}$	$\frac{W_A}{W_B}$ OBS	$\frac{OBS}{PRED}$
Penta	0.038	4.6×10^{-5}	1×10^{-3}	0.04	1
Phenol	0.25	10^{-6}	4×10^{-6}	7×10^{-4}	3×10^{-4}
Naphthalene	0.18	4×10^{-6}	3×10^{-5}	8×10^{-3}	5×10^{-2}
Anthracene	0.013	3×10^{-6}	2×10^{-4}	10^{-3}	9×10^{-2}
Fluorene	1.5×10^{-3}	4×10^{-6}	3×10^{-3}	2×10^{-3}	1.2
Phenanthrene	5.2×10^{-3}	10^{-5}	2×10^{-3}	2×10^{-3}	0.4
Pyrene	1.4×10^{-4}	4×10^{-6}	3×10^{-2}	2×10^{-3}	1.3

TABLE 5-15. CREOSOTE PAN EVAPORATION -- STEAM DISTILLATION MODEL

		Test 2		Test 3	
	$\frac{W_A}{W_B}$ PRED	$\frac{W_A}{W_B}$ OBS	$\frac{OBS}{PRED}$	$\frac{W_A}{W_B}$ OBS	$\frac{OBS}{PRED}$
Penta	0.041	9×10^{-5}	2×10^{-3}	3.7×10^{-6}	9×10^{-5}
Phenol	0.24	2×10^{-5}	8×10^{-5}	7.9×10^{-5}	3.3×10^{-4}
Naphthalene	0.16	2.7×10^{-4}	1.7×10^{-3}	3.7×10^{-3}	0.023
Anthracene	0.013	4.3×10^{-5}	3×10^{-3}	9.2×10^{-5}	0.007
Fluorene	1.6×10^{-3}	1.5×10^{-4}	0.096	7.4×10^{-4}	0.46
Phenanthrene	2.3×10^{-3}	1.3×10^{-4}	0.056	2.6×10^{-4}	0.11
Pyrene	1.2×10^{-4}	2.1×10^{-5}	0.18	1.7×10^{-5}	0.16

Mass Transfer Limited Emissions--

The concentration of component A in the gas phase falls as the concentration in the solution falls; the emission rate also falls, assuming the water evaporation rate remains constant. Given sludge with a high concentration of component A (an infinite source), material dissolves from this source into solution at an increasing rate as the concentration in solution falls. At a certain concentration, transfer rate from source to water is balanced by the rate of transfer from water to air.

Over an interval of time, the average concentration of component A emitted (assuming evaporation volume change is negligible) is given by:

$$\frac{V_l(C_{AS} - C_A)}{V_g} = C_{Ag} \qquad (4)$$

where V_l = volume of wastewater in evaporator (liters)

C_{AS} = saturation concentration of A (mg/l)

C_A = steady state concentration of A (mg/l)

V_g = volume of water evaporated (liter)

C_{Ag} = concentration of component A in emission (mg/l)

From the analytical data, only the creosote pan evaporator sludge contains sufficient material to act as an infinite source.

Pure Static Liquid Evaporation--

Pure static liquid evaporation models are based on gas phase diffusion calculations assuming that the source concentration is constant and the driving force for transfer is pure vapor pressure. The classical approach for determining vapor pressure (and therefore gas phase concentration) is to use Raoult's law for ideal solution:

$$p_A = p_A^o x_A \qquad (5)$$

where P_A = partial pressure of component A

P_A^o = partial pressure of pure component A at the temperature of the solution

X_A = mole fraction of component A in solution

This approach assumes that the solution is ideal, that solute and solvent do not interact, that the solute and solvent molecules are approximately the same size, and that the concentration of the solute is well below saturation. When such is not the case (as is obvious in the pan evaporation system), a regular solution theory is invoked; an activity coefficient of the solute-solvent system is incorporated into the formula:

$$P_A = P_A^o X_A \gamma_A \tag{6}$$

The activity coefficient, γ, is a measure of the departure from the ideal (Raoult's law). For $\gamma > 1$, there are positive deviations, and for $\gamma > 1$, negative deviations. Hydrocarbon/water systems almost universally have positive deviations. Predicted deviations for the system studied here are orders of magnitude greater than one (3).

Flash Evaporation--

When wastewater is flash-evaporated, the concentration of a given component in the gas phase equals its concentration in the liquid phase. The emission rate is equal to the evaporation rate of water times the component concentration in the water.

5.2.2 <u>Comparison to Predictions</u>

The predicted emission concentrations for each mechanism during the six tests is given in table 5-16. These values are for naphthalene, a major component in both the creosote and the penta streams. The observed values are

TABLE 5-16. COMPARISON OF PAN EVAPORATOR MODELS FOR NAPHTHALENE (g/sm^3)

Mode / Test number	Penta evaporator 2	Penta evaporator 3	Penta evaporator 4	Creosote evaporator 2	Creosote evaporator 3	Creosote evaporator 4
Pure steam distillation	130	130	130	120	120	130
Limited mass transfer (sludge to water to gas)	9	14	16	3.2	3.4	3.1
Flash evaporation	3×10^{-4}	7×10^{-5}	2×10^{-4}	1×10^{-2}	7×10^{-3}	5×10^{-3}
Pure static liquid (ideal solution)	7.7×10^{-6}	1.9×10^{-6}	5.6×10^{-6}	2.2×10^{-4}	1.7×10^{-4}	1.1×10^{-4}
Pure static liquid (regular solution)	1.5	0.4	1.1	44	34	22
Observed	2×10^{-3}	3×10^{-3}	6.0	0.2	2.8	2.2

much higher than is predicted by classical evaporation theory, but lower than the predicted steam distillation values.

5.3 CONCLUSIONS

The results of this study conclusively confirm that almost all organic species analyzed in the wastewater stream are emitted to the atmosphere upon pan evaporation. Furthermore, the bulk of the organics is emitted. Finally, the emission rate of the organics in toto and of specific components is cyclic.

This cyclic nature is the result of the once-a-day charging of the evaporators from the oil/water separators. The total amount of organics emitted strongly depends on the effectiveness of the oil/water separator.

Sludge generation is approximately 2.5 metric tons/year/evaporator, about half of which is returned to the process. The remainder is disposed of, usually by landfill in 55-gal drums.

SECTION 6

CHARACTERIZATION OF MULTIMEDIA EMISSIONS FROM SPRAY EVAPORATION OF WOOD PRESERVING WASTEWATERS

This field test program was conducted at a wood treating plant utilizing spray pond evaporation to reduce its wastewater volume. The program was designed to determine the organic emissions from the spray pond and the resulting sludge layer, as well as from the wastewater input. Each stream was qualitatively and semiquantitatively analyzed for organic compounds, including volatile organics, chlorinated dibenzo-p-dioxins, chlorinated dibenzofurans, chlorinated phenolic compounds, and polynuclear aromatic hydrocarbons.

6.1 PROGRAM DESCRIPTION

This program focused on determining if organic emissions were discharged to the air during evaporation and if the transport mechanism could be established. Possible mechanisms were simple evaporation or aerosol drift. In addition, the cryogenic sampling system and resin trapping methods were compared.

6.1.1 Test Site

The wood treating facility selected for field sampling employed two treating cylinders using a closed steaming process. Both cylinders could treat wood using penta formulations; one cylinder also could use creosote. Wood products treated at the plant consisted almost entirely of Southern yellow pine in the form of utility poles and lumber.

Wastewater and byproducts generated from the treating process were discharged into discrete oil/water separators. Each separator held 10,000 gal. Primary separation was carried out as a batch process with an average retention time of 18 hours. The tanks were operated manually, and the recovered treating formulation was returned to the appropriate bulk storage tank. Creosote wastewater was discharged directly into the spray pond. Wastewater from the penta oil/water separator was further treated by a three-zone gravity separator using a skimming device to recover any remaining penta residue, after which the wastewater was discharged into the spray pond.

The spray pond consisted of an unlined pond with a pumping station and seven spray nozzles. The sprays were operated 24 hrs/day unless local wind conditions caused excessive drifting of the spray.

6.1.2 Field Test Program

The sampling program conducted included each of these tests:

- Determination of atmospheric characteristics at the spray pond
- Air emission sampling at the spray pond using:
  - Cryogenic U-tubes
  - Tenax traps
  - XAD-2 cartridges
- Liquid grab samples of spray pond wastewater
- Solids samples of spray pond sludge and soil samples in areas near the spray pond

Table 6-1 presents a summary of the field test matrix for the sampling period.

The air emission samples were collected using a sampling train developed by the University of Arkansas. A complete description of this unit is contained in appendix B. The train was used to collect cryogenics (water

TABLE 6-1. SUMMARY OF SAMPLES COLLECTED

Sample	Air samples -- spray pond non-isokinetic sampling	Liquid samples -- composited grab sampling	Solid samples -- composited sludge sampling
1	4-XAD2, cryogenics and field volatiles using Tenax	1-composite	1-composite
2	4-XAD2, cryogenics and field volatiles using Tenax	1-composite	1-composite
3	4-XAD2, cryogenics and field volatiles using Tenax	1-composite	1-composite

and organics collected in a cold trap), nonvolatile organics in XAD-2 resin traps, and volatile organics in Tenax traps. Temperature and wind vector information also was collected.

6.1.3 Process Description

The data for the pond evaporation study is given in table 6-2.

6.2 DISCUSSION OF RESULTS

Emission rates could not be determined due to the detection limits of the sampling and analytical methodology. While the University of Arkansas (UA) methodology is currently the best approach to determining organic emission rates from surface waters, the physical limits of spray pond evaporation and the sampling system prevent the detection of low and medium volatile compounds.

The best ambient air monitoring instrumentation available under optimum laboratory conditions can obtain levels of sensitivity to about 10 ppb (v/v)

TABLE 6-2. DATA FOR POND EVAPORATION

Component	Pond sludge (μg/g)	Waste-water input (μg/g)	Pond water recycle (μg/g)	Test 4 (total μg)	All others (total μg)	
Pentachlorophenol	15,000	1,100	15	41, 5.2, 4.0	ND*	
Phenol	50	48	0.1		ND	ND
Fluoranthene	5,800	23	3	1.4, ND, ND	ND	
Naphthalene	1,500	120	4		ND	ND
Benzo(a)anthracene	2,600	ND	0.4		ND	ND
Chrysene	2,000	ND	0.6		ND	ND
Anthracene	2,700	ND	0.7		ND	ND
Fluorene	5,600	58	1.7		ND	ND
Phenanthrene	9,000	67	6.4	1.7, ND, ND	ND	
Pyrene	4,400	15	1.6	1.1, ND, ND	ND	
Octachloro dibenzodioxin	2.1	--**	--		--	--
Chloro dibenzofurans	1.4	--	--		--	--
Oil and grease	--	--	160		--	--

*ND = Not detected
**-- = Not analyzed

or methane equivalents of about 10 pg per analytical injection: this is for total organics, not individual components. Normal field monitoring instruments are good to about 1 ppm (v/v) for total organics. The QA procedure allows field samples to be analyzed at concentrations 10 times lower than the most sensitive methods or 1,000 times lower than the usual methods. For a compound such as phenol, this means a detection limit of about 1 to 5 ppb (v/v) in the gas phase of individual components.

The different molecular weights of the compounds under study make it easier to work with concentration units of weight to sample volume. This gives the following sensitivities for the three sampling methodologies:

- Ambient monitoring -- 10 ng/l of methane equivalent for total organics (no speciation)
- Field monitoring -- 1 μg/l of methane equivalent for total organics (no speciation)
- UA methodology (FID) -- 0.5 ng/l of individual components

Use of gas chromatography/mass spectrometry (GC/MS) with the UA sampling methodology decreases the sensitivity to about 50 ng/l. The sample volumes for the two standard methods are fixed by the instrumentation, while the sample volume of the UA system is limited by the moisture content of the gas stream: water vapor frozen out in the collection device eventually stops sample flow.

In this study we drew 5 to 10 times the recommended amount of sample, increasing our sensitivity by approximately one order of magnitude.

Raoult's law of partial pressure predicts concentrations of penta in the range of 3×10^{-3} pg/l. Pure penta exhibits concentrations of 3 ng/l (300 ng/sm^3). Although the normal sampling location for the UA system is at the water surface, this test required taking the samples on the berm, about 3 ft above water level. To offset the subsequent dilution, the samplers were run as long as possible (until the traps froze up). The results were detection limits only 2 to 3 times less than the maximum possible (see table 6-3), not nearly enough to make up for dilution. Dilution would be at least 10- to 20-fold over a distance of 2 ft.

In conclusion, the methodology was insufficient to determine emissions off the ponds.

TABLE 6-3. DETECTION LIMITS -- POND EVAPORATION

TABLE 6-3. DETECTION LIMITS -- POND EVAPORATION

Test	Flow (ml/min)	Elapsed time (min)	Temperature (^{o}C)	Volume (sm^3)	Detection limit ppt (w/v): GC/MS (ng/sm^3)	Detection limit ppt (w/v): GC/FID (ng/sm^3)	Test type
1	66	23	8.5	1.6×10^{-3}	640	6.4	Cryogenic blank
2	66	135	6.4	9.4×10^{-3}	110	1.1	Tenax + XAD blank
3	66	180	8	13.0×10^{-3}	80	0.8	Tenax
4	66	90	12	6.1×10^{-3}	160	1.6	Cryogenic
5	66	42	12	2.9×10^{-3}	350	3.5	Cryogenic
6	66	69	8	4.8×10^{-3}	210	2.1	Cryogenic
7	66	94	3	6.6×10^{-3}	150	1.5	XAD
8	66	120	7	8.3×10^{-3}	120	1.2	XAD
9	66	120	14	8.1×10^{-3}	120	1.2	XAD
10	66	122	16	8.2×10^{-3}	120	1.2	Tenax
11	66	120	8	8.3×10^{-3}	120	1.2	Tenax

Maximum penta concentration = $\mu g/sm^3$ (30 ppb v/v)
Analytical sensitivity
  Field GC/TVOC = 1 ppm
  GC/MS concentrate = 1 μg/sample (1 ng injected)
  GC/FID concentrate = 10 ng/sample (10 pg injected)

SECTION 7

CHARACTERIZATION OF EMISSIONS FROM THE DISPOSAL OF WOOD PRESERVING WASTES IN AN INDUSTRIAL BOILER

The Resource Conservation and Recovery Act (RCRA) is expected to cause some generators of hazardous wastes to dispose of their wastes within plant boundaries. One disposal option is the thermal destruction of the waste in a steam boiler. This field test program was conducted at a wood preserving facility using a pile-burning watertube boiler cofiring a mixture of wood waste and penta/creosote wastewater. The program was designed to determine the destruction and removal efficiencies of the organic compounds in the wastewater. Input materials (the wood waste and sludge) and output materials (mechanical hopper ash, baghouse ash, and bottom ash) were analyzed, and pertinent data for a material balance evaluation were collected. All samples were qualitatively and semiquantitatively analyzed for organic compounds, including chlorinated phenols, chlorinated dibenzo-p-dioxins, chlorinated dibenzofurans, and polynuclear aromatic hydrocarbons.

7.1 PROGRAM DESCRIPTION AND RESULTS

This program focused on the gaseous emissions discharged from the stack and the ash streams resulting from combustion and pollution control. Making material balance estimates was difficult since ash and fuel flowrates were not metered by the operator. However, estimates were made of each stream, and the destruction and removal efficiencies were evaluated.

7.1.1 Test Site

The wood treating facility selected for field sampling employs six retorts using a steaming process to treat a variety of domestic and imported wood products. The process can treat wood with penta, creosote, or waterborne preservative formulations.

Wastewater and byproducts generated from the individual treating processes are handled by discrete oil/water separators. The recovered preservative fractions are returned to bulk storage tanks for reuse in the process. Separated sludges and wastewater are routed to a storage tank; when quantity is sufficient to ensure economic handling, the wastes go to the steam boiler for disposal. Figure 7-1 presents a schematic of the plant wastewater/preservative recovery system. An estimated 5,000 to 8,000 gal/day of wastewater is generated during normal treating operations.

The boiler manufactured by Wellons Company was designed to produce 40,000 lb/hr of steam for space heat, the treating cycle, and other plant operations. The boiler unit, consisting of both a cell and a furnace, could be fired using both or fired separately, depending on plant process demand.

The boiler fuel supply system consisted of transfer and metering conveyors, wet and dry fuel silos, two metering bins for cell and furnace, and a constantly running screw conveyor to charge the fuel to the cell and furnace for burning. Both screw conveyors were modified to allow hog fuel to be mixed with sludge and/or wastewater from the treating plant. The cell also was equipped with a ram charging device for loading irregular-shaped and oversized wood scrap into the boiler.

7.1.2 Field Test Program

The sampling program conducted included each of these tests:

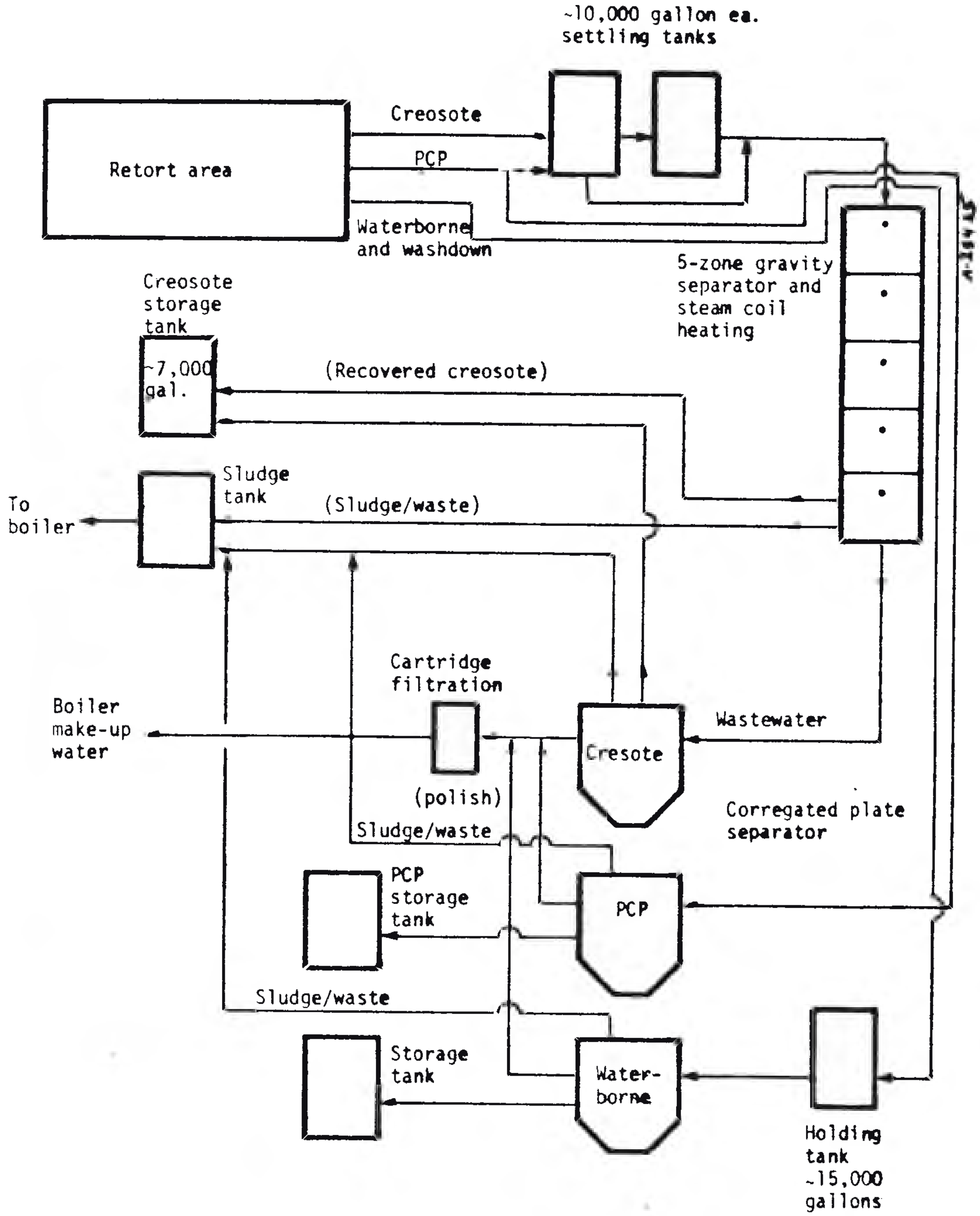

Figure 7-1. Schematic of plant wastewater/preservative recovery system.

- Determination of preliminary gas stream characteristics
- Isokinetic source sampling of boiler flue gas
- Total hydrocarbon determination of boiler flue gas
- Specific low-molecular-weight hydrocarbon determination of flue gas using gas chromatography (GC)
- Composite sampling of:
  - -- Boiler bottom ash
  - -- Multicone hopper ash
  - -- Wood waste fuel
  - -- Sludge wastewater fuel
- Grab sampling of:
  - — Baghouse ash
  - -- Bulk penta in aromatic treating oil
  - — Bulk creosote

The sample collection matrix is shown in table 7-1. The air samples were collected using an EPA Method 5 sampling train with XAD-2 resins for nonvolatile organic emissions. Volatile emissions were determined using field GC methods.

7.1.3 Data Presentation -- Organics and Inorganics

The concentrations of organic components in the various samples are shown in table 7-2. The corresponding concentrations of trace elements are given in table 7-3. Concentration units are in μg/g (ppm w/w) for the solids and liquid (sludge), and in units of $\mu g/sm^3$ (ppt w/v at $23^{o}C$ and 1 atm). Components not detected are listed as less than (<) values if the number is a direct analytical measurement or as not detected (ND) if the value is calculated (i.e., averaged or requiring independent test data). NA means the

TABLE 7-1. SAMPLE COLLECTION MATRIX

	Air samples	Solid samples			
Sample number	Outlet stock	Wood waste and sludge	Boiler bottom ash	Mech. hopper ash	Baghouse ash
1	1-XAD, GC	1-composite	1-grab	1-composite	1-grab
2	1-XAD, GC	1-composite	1-grab	1-composite	1-grab
3	1-XAD, GC	1-composite	1-grab	1-composite	1-grab
4	1-XAD, GC	1-composite	1-grab	1-composite	1-grab

Columbus Ohio

TABLE 7-2. CONCENTRATIONS OF ORGANIC COMPONENTS IN INCINERATOR SAMPLES

	Feed sludge (μg/g)				Bottom ash (μg/g)				Mechanical hopper (μg/g)				Baghouse dust (μg/g)				Stack gas (μg/sm³)			
Sample test	2	3	4	Ave	2	3	4	Ave	2	3	4	Ave	2	3	4	Ave	2	3	4	Ave
Pentachlorophenol	470	260	80	270	0.5	0.5	0.5	0.5	0.05	0.5	7.4	2.7	1.0	1.0	1.0	1.0	ND	ND	ND	ND
Phenol	1200	1000	1400	1200	0.1	0.8	0.6	0.8	0.1	0.1	0.1	0.1	0.5	0.2	0.3	0.3	4.1	2.7	2.3	3.0
Fluoranthene	2200	340	170	1355	92.0	15.0	1.4	36.1	0.5	0.6	1.7	0.9	0.7	0.2	6.2	2.4	ND	ND	ND	ND
Naphthalene	1300	1000	560	953	10.0	18.0	9.6	12.5	10.0	6.5	2.2	6.2	10.0	3.9	5.1	6.3	570.2	150.5	161.3	294.0
Benzo(a)anthrocene	160	120	27	102	7.6	0.6	0.1	2.8	<0.1	0.1	0.1	0.1	0.5	0.2	0.5	<0.4	ND	ND	ND	ND
Benzo(a)pyrene	<20	30	<10	20	1.4	0.1	0.1	0.5	<0.1	0.1	0.1	0.1	0.5	0.2	0.5	<0.4	ND	ND	ND	ND
Benzo fluoranthene	52	64	14	43	9.3	0.9	0.1	3.4	<0.1	0.1	0.1	0.1	0.5	0.2	0.5	<0.4	ND	ND	ND	ND
Cryrene	180	120	28	109	1.2	0.7	0.1	0.7	<0.1	0.1	0.3	0.2	0.5	0.2	0.5	<0.4	ND	ND	ND	ND
Acenaphthylene	130	68	24	74	4.4	3.0	0.1	2.5	<0.1	0.1	0.1	0.1	0.5	0.2	0.5	<0.4	ND	ND	ND	ND
Anthracene	760	250	92	367	4.5	1.0	0.2	1.9	<0.1	0.1	0.2	0.1	0.5	0.2	0.5	0.4	ND	ND	ND	ND
Fluorene	1200	420	180	600	0.6	0.8	0.1	0.5	<0.1	0.1	0.1	0.1	0.5	0.2	0.5	0.4	ND	ND	ND	ND
Phenanthrene	1800	590	330	813	24.0	31.0	3.0	19.3	0.6	0.5	0.4	0.5	6.9	3.0	7.3	5.7	ND	ND	ND	ND
Pyrene	1200	310	140	550	29.0	7.9	0.4	12.4	<0.1	0.1	0.4	0.2	0.5	0.2	0.5	0.4	ND	ND	ND	ND
Benzenes	1	<1	<1	1	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	ND	ND	ND	ND
Toluene	12	3.7	9	8.2	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	ND	ND	ND	ND
Ethylbenzene	17	5.7	10	10.9	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	ND	ND	ND	ND

TABLE 7-3. INORGANIC TRACE ELEMENT COMPOSITIONS IN INCINERATOR SAMPLES

Sample	Test	As	Be	Cd	Zn	Cr	Cu	Pb	Ni	Ag	Sb	Hg	Se	Tl
Feed sludge	2	6.8	0.001	<0.02	10.0	2.7	36	<1	<0.2	<0.06	<0.05	0.01	<0.05	<0.001
	3	3.5	$<9 \times 10^{-4}$	<0.02	7.0	2.6	48	<1	<0.2	<0.06	0.25	0.01	0.05	<0.001
	4	8.1	$<9 \times 10^{-4}$	<0.02	3.0	2.0	19	<1	<0.2	<0.06	0.16	0.02	0.10	<0.001
	Ave	6.1	ND	ND	6.6	2.5	34	ND	ND	ND	0.13	0.013	0.05	ND
Bottom ash	2	0.35	1.0	<0.02	2.0	1.0	29	<1	0.6	<0.06	<5.0	1.0	<5.0	<0.11
	3	40.5	0.7	<0.02	5.0	0.6	57	<1	0.5	<0.06	<5.0	2.0	10.0	<0.1
	4	73.0	1.0	<0.02	8.0	1.1	29	<1	0.4	<0.06	<5.0	0.9	10.0	<0.1
	Ave	38.0	0.9	ND	5.0	0.9	38	ND	0.5	ND	ND	1.3	10.0	ND
Mechanical hopper ash	2	0.02	2.0	0.1	90.0	1.9	85	100	0.3	<0.06	<5.0	3.0	<5.0	<0.1
	3	6.5	0.9	<0.02	40.0	2.0	120	10	0.3	<0.06	<5.0	4.0	<5.0	<0.1
	4	0.88	0.9	<0.02	30.0	1.8	70	10	0.2	<0.06	<5.0	2.0	<5.0	<0.1
	Ave	0.5	1.3	0.03	53.0	1.9	92	40	0.3	ND	ND	3.0	ND	ND
Baghouse dust	2	0.53	0.4	0.3	750.0	2.9	230	1500	0.4	0.1	25.0	5.0	10.0	<0.1
	3	11.4	0.4	0.4	750.0	4.4	305	1500	0.4	0.1	38.0	12.0	10.0	<0.1
	4	49.0	0.2	0.3	500.0	3.4	225	1200	<0.2	0.1	28.0	11.0	10.0	<0.1
	Ave	20.0	0.3	0.3	700.0	3.5	253	1400	0.3	0.1	30.0	9.0	10.0	ND

Units -- µg/g (ppm w/w)

component was not analyzed for.

The air emission rates for naphthalene and phenol are summarized in table 7-4. Other components are not listed because they were not detected (detection limits are $<10^{-5}$ g/sec). Stack sampling data are summarized in appendix C.

7.2 MATERIAL BALANCE AROUND INCINERATOR

To determine the destruction efficiency of the hazardous waste components, a material balance around the boiler facility was generated. The particular components of interest could be used because an unknown fraction was being destroyed. Therefore, an indestructable material was used as a tracer. The following steps were taken:

- Identification of input and output streams
- Determination of stream flowrates
- Calculation of organic component mass flowrates
- Calculation of destruction efficiency

The streams were identified as the:

- Feed sludge
- Bottom ash
- Mechanical hopper ash
- Baghouse dust
- Stack emissions

The working equation for the material balance is given as:

$$R_f \, C_{fj} = \Sigma \, R_i \, C_{ij} \qquad (7)$$

TABLE 7-4. RATES OF DISCHARGE AND EFFICIENCY OF DESTRUCTION FOR NAPHTHALENE AND PHENOL

		Feed (g/sec)	Bottom ash (g/sec)	Mech. hop. (g/sec)	Baghouse (g/sec)	Gas (g/sec)	Total out (g/sec)	Efficiency (percent)
Test 2								
	Naphthalene	0.25	1×10^{-5}	7.6×10^{-6}	2×10^{-7}	3.9×10^{-3}	3.9×10^{-3}	98.4
	Phenol	0.23	$<1 \times 10^{-7}$	$<8 \times 10^{-8}$	$<8 \times 10^{-9}$	2.9×10^{-5}	2.9×10^{-5}	99.99
	Solid rate	189	1.01	0.76	0.017	(6.85)[a]		
Test 3								
	Naphthalene	0.19	1.3×10^{-5}	8.5×10^{-6}	8.2×10^{-8}	1×10^{-3}	1×10^{-3}	99.5
	Phenol	0.19	6×10^{-7}	1.3×10^{-7}	4.2×10^{-9}	$<1.9 \times 10^{-5}$	$<2 \times 10^{-5}$	>99.99
	Solid rate	189	0.74	1.3	0.021	(6.85)[a]		
Test 4								
	Naphthalene	0.11	2.9×10^{-6}	1.8×10^{-8}	1.1×10^{-7}	1.1×10^{-7}	1.1×10^{-3}	99.0
	Phenol	0.27	1.8×10^{-7}	$<8 \times 10^{-10}$	6.3×10^{-9}	1.6×10^{-5}	1.6×10^{-5}	99.99
	Solid rate	189	0.30	0.35	0.008	(6.99)*		

Assumptions: Feed rate, all cases = 189 g/sec sludge; sludge is source of metals; all Zn, Cr, Cu comes out in solids.

*Sm^3/sec (23°C and 1 atm)

= 1,2 %

2,061

Ave ~ 1.06%

where

R_f = feed rate of sludge

C_{fj} = concentration of j^{th}component in the feed

R_i = rate of discharge of i^{th} stream

C_{ij} = concentration of j^{th} component in i^{th} stream

Measured rates were available for the feed and the stack gas emissions. The feed rate was 2.7 gal/min with a density of 1.1 g/ml or 189 g/sec. The gas volume ranged from 6.85 to 6.99 sm^3/sec (23^oC and 1 atm). The grain loading was not detectable ($<10^{-3}$ g/sm^3 or $<10^{-2}$ g/sec), so solids in the gas stream were negligible.

Rates for the three ash streams were not directly measurable; these were obtained using the trace element analyses and a corresponding set of three simultaneous equations generated from (7). All the given element was assumed to be introduced in the feed with none emitted out the stack. The chosen elements, zinc, chromium, and copper, were relatively high in the feed with relatively low volatility. An unmeasured portion possibly introduced with the wood chips is partially offset by the unmeasured air emissions.

The matrix of these equations is set up in table 7-5 with a solution for the three unknown rates. The results for the three tests are consistent and in good agreement. Using these calculated rates, the flowrates of naphthalene and phenol (the only observed organic emissions) were derived and presented in table 7-4. The destruction efficiency also is presented, as calculated from the equation:

$$E = \frac{R_f\ C_{f,j} - \sum R_i,\ C_{i,j}}{R_f\ C_{f,j}} \times 100 \qquad (8)$$

TABLE 7-5. CALCULATION OF RATES OF GENERATION OF SOLIDS

		Bottom ash $C_{1,j}$ (µg/g)	Hopper ash $C_{2,j}$ (µg/g)	Baghouse dust $C_{3,j}$ (µg/g)	Feed R_f, $C_{f,j}$ (µg/sec)
Test 2					
	Zn	2	750	90	1,890
	Cr	1	2.9	1.9	510
	Cu	29	230	85	6,890
	R_i (g/sec)	1.0	0.017	0.76	
Test 3					
	Zn	5	750	40	1,320
	Cr	0.6	4.4	2.0	491
	Cu	57	305	120	9,070
	R_i (g/sec)	0.74	0.021	1.3	
Test 4					
	Zn	8	500	30	567
	Cr	1.1	3.4	1	378
	Cu	29	225	70	3,590
	R_i (g/sec)	0.30	0.008	0.35	

7.3 CHLORODIBENZOFURANS AND CHLORODIOXINS

Chlorodibenzofurans and chlorodioxins are abbreviated CDF and CDD, respectively. The abbreviations for the various chlorinated homologs are listed in table 7-6, along with the possible number of isomers for each. The analytical results are presented in tables 7-7 to 7-12.

For each of the listed homologs of CCD and CDBF, typically only a single isomer was available for calibration. The total number of isomers was deduced by comparing the GC/MS properties of the standard to those unknown compounds exhibiting similar properties. However, since not all isomers of a given group were available for calibrating retention times, a given mass

TABLE 7-6. SUMMARY OF ABBREVIATIONS FOR CHLORODIBENZOFURAN AND CHLORODIBENZODIOXINS

Abbreviations	Name	Possible isomers
MCDF	Monochlorodibenzofuran	4
DCDF	Dichlorodibenzofuran	16
TrCDF	Trichlorodibenzofuran	28
TCDF	Tetrachlorodibenzofuran	53
PCDF	Pentachlorodibenzofuran	28
HxCDF	Hexachlorodibenzofuran	16
HpCDF	Heptachlorodibenzofuran	4
OCDF	Octachlorodibenzofuran	1
MCDD	Monochlorodibenzodioxin	2
DCDD	Dichlorodibenzodioxin	10
TrCDD	Trichlorodibenzodioxin	14
TCDD	Tetrachlorodibenzodioxin	22
PCDD	Pentachlorodibenzodioxin	14
HXCDD	Hexachlorodibenzodioxin	10
HPCDD	Heptachlorodibenzodioxin	2
OCDD	Octachlorodibenzodioxin	1

TABLE 7-7. CHLORODIBENZOFURAN AND CHLORODIBENZODIOXIN ANALYTICAL RESULTS FOR TREATMENT OIL (4.5 PERCENT PENTA IN OIL)

CDD/CDF*	Total no. of apparent isomers**	Total detected*** (ng/g)	Minimum detectable concentration (ng/g)
MCDF	4	2	0.4
DCDF	2	2	0.8
TrCDF	4	10	1.2
TCDF	5	18	0.1
PCDF	5	137	1
HxCDF	5	1813	1
HpCDF	2	114	1
OCDF	1	711	3
MCDD	2	1.5	0.4
DCDD	2	2	0.8
TrCDD	2	3.5	1.2
TCDD	-	1.1	0.5
PCDD	6	33	0.3
HxCDD	4	574	1
HpCDD	2	256	1
OCDD	1	3996	3

*See table 7-6 for summary of nomenclature
**See text
***Not corrected for recovery, these concentrations represent minimum values

TABLE 7-8. CHLORODIBENZOFURAN AND CHLORIDIBENZODIOXIN ANALYTICAL RESULTS FOR DAY 2 COMPOSITE SLUDGE LIQUID

CDD/CDF*	Total no. of apparent isomers**	Total detected*** (ng/g)	Minimum detectable concentration (ng/g)
MCDF	4	0.6	0.2
DCDF	0	0	0.3
TrCDF	0	0	0.7
TCDF	0	0	0.1
PCDF	1	0.3	0.2
HxCDF	2	0.8	0.5
MCDD	1	0.2	0.2
DCDD	0	0	0.3
TrCDD	0	0	0.7
TCDD	0	0	0.9
PCDD	3	0.6	0.3
HxCDD	4	2.5	0.5

5 [illegible]

*See table 7-6 for summary of nomenclature
**See text
***Not corrected for recovery, these concentrations represent minimum values

TABLE 7-9. CHLORODIBENZOFURAN AND CHLORODIBENZODIOXIN ANALYTICAL RESULTS FOR DAY 4 COMPOSITE SLUDGE LIQUID

CDD/CDF*	Total no. of apparent isomers**	Total detected*** (ng/g)	Minimum detectable concentration (ng/g)
MCDF	3	0.7	0.2
DCDF	0	0	0.4
TrCDF	0	0	0.9
TCDF	0	0	0.05
PCDF	1	0.5	0.2
HxCDF	3	8	2
HpCDF	2	7	1
OCDF	1	2	1
MCDD	1	0.6	0.2
DCDD	1	0.4	0.4
TrCDD	0	0	0.9
TCDD	0	0	0.9
PCDD	0	0	1
HxCDD	3	10	1
HpCDD	2	70	1
OCDD	1	225	1

324.2 ng/g

*See table 7-6 for summary of nomenclature
**See text
***Results corrected for recovery

TABLE 7-10. CHLORODIBENZOFURAN AND CHLORODIBENZODIOXIN ANALYTICAL RESULTS FOR DAY 2 COMPOSITE ASH

CDD/CDF*	Total no. of apparent isomers**	Total detected*** (ng/g)	Minimum detectable concentration (ng/g)
MCDF	3	75	0.1
DCDF	8	25	0.3
TrCDF	8	15	0.6
TCDF	7	7	0.5
PCDF	5	8	1
HxCDF	5	5	1
HpCDF	2	6	1
OCDF	1	2	1
MCDD	1	1	0.1
DCDD	4	5	0.3
TrCDD	5	2	0.6
TCDD	4	3.4	0.2
PCDD	5	32	1
HxCDD	5	81	1
HpCDD	2	117	1
OCDD	1	198	1
		592 ng/gm	

*See table 7-6 for summary of nomenclature
**See text
***Results corrected for recovery

TABLE 7-11. CHLORODIBENZOFURAN AND CHLORODIBENZODIOXIN ANALYTICAL RESULTS FOR DAY 3 COMPOSITE ASH

CDD/CDF*	Total no. of apparent isomers**	Total detected*** (ng/g)	Minimum detectable concentration (ng/g)
MCDF	3	90	0.1
DCDF	8	7.5	0.3
TrCDF	6	20	0.6
TCDF	8	1.2	0.05
PCDF	5	0.7	0.1
HxCDF	2	1	0.3
HpCDF	2	1.6	0.6
OCDF	1	1.2	1
MCDD	1	2	0.1
DCDD	5	1	0.3
TrCDD	5	5	0.6
TCDD	-	0.8	0.2
PCDD	5	2.6	0.1
HxCDD	1	8.7	0.3
HpCDD	2	42	1
OCDD	1	96	1
		282 ng/gm	

*See table 7-6 for summary of nomenclature
**See text
***Results corrected for recovery

TABLE 7-12. CHLORODIBENZOFURAN AND CHLORODIBENZODIOXIN ANALYTICAL RESULTS FOR DAY 4 COMPOSITE ASH

CDD/CDF*	Total no. of apparent isomers**	Total detected*** (ng/g)	Minimum detectable concentration (ng/g)
MCDF	3	5	0.1
DCDF	10	8	0.3
TrCDF	11	17	0.6
TCDF	8	3	0.1
PCDF	5	3	0.3
HxCDF	4	1.8	0.4
HpCDF	0	0	2
OCDF	0	0	1
MCDD	2	0.7	0.1
DCDD	4	0.5	0.3
TrCDD	4	6	0.6
TCDD	6	3.3	0.2
PCDD	4	6	0.3
HxCDD	3	10	0.4
HpCDD	2	4	2
OCDD	1	1	0.8

70 ng/[illegible]

*See table 7-6 for summary of nomenclature
**See text
***Results corrected for recovery

chromatographic peak does not necessarily correspond to a single isomer of a given class; such peaks may represent more than one isomer. Hence, the terminology "apparent isomers."

No CDF's or CDD's were detected in the air emissions. The detection limits were <10 $\mu g/sm^3$ (10 ppt w/v). CDF's were detected in the hopper and baghouse dust, but not in the bottom ash; the converse was true for the CDD. Although there was an apparent generation of TCDD's, data analysis placed this in some doubt. Using OCDD as a tracer, the apparent dilution from the oil to the sludge was about x200 or 5 x 10^{-3} ng/g total TCDD's in the sludge (well below the detection limit of the analytical methodology). The mass flowrate of TCDD's into the boiler (from previous material balance results) is about 1 ng/sec. The bottom ash generation rate is about 0.6 g/sec with a TCDD concentration of about 2 ng/g or a TCDD output rate of 1.2 ng/sec. The sampling, analytical, and data reduction error bounds are large enough to preclude stating that TCDD is generated. It can be said that the apparent destruction of TCDD is minimal.

Contradiction

What is of concern is that, while 2,3,7,8 TCDD does not appear to be present in the sludge and oil, it does appear to be present in the ash. This suggests formation by thermal isomerizations, requiring a much deeper study of these samples.

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SECTION 8

EVALUATION OF FUGITIVE EMISSION SOURCES

For the purposes of this program, fugitive emissions are defined as emissions from:

- Treating cylinder spillage and drippage
- Vapors released from the treating cylinder during unloading and charging operations
- Vacuum vent exhaust during the treating cycle
- Transfer of treating solution formulations from valves, fittings, or open processing vessels

These emission sources are of concern because of the opportunities for employees to contact directly the toxic compounds.

When the treating cylinder (retort) is opened, any treating solution left in the vessel may spill onto the ground. If the retort is surrounded by a spill beam, the treating solutions are recovered and recycled to the system. However, if the treating solution is allowed to fall onto the ground, housecleaning activities could accumulate hazardous waste material.

Low-molecular-weight organic compounds vaporize in the retort during the high-temperature preservative application. During charge changes, these organics are released as fugitive emissions through the open door of the retort, forming a dense white plume. The wood removed from the retort also emits material as a white plume that may exceed 40 percent opacity after

20 min. Qualitative and semi-quantitative organic analyses for specific pollutants in these emissions were expected to show the presence of benzene, toluene, phenoi, and similar volatile and low-molecular-weight compounds.

Emissions from the vacuum exhaust and other retort vents also are of concern. Source tests at one mill measured 2.2 g/m^3 (0.95 grain/scf) of aerosol in 12.5 m^3/min (440 scfm) of gas from a vacuum pump vent. Steam conditioning released 44 g/m^3 of aerosol in a 13 m^3/min stream.

Finally, while fugitive emissions from preservative handling, transport, leaks, and valves can occur, no qualitative or quantitative data is available to characterize such emissions.

This section presents the component speciation results from fugitive emissions tests conducted at a wood preserving facility. Emissions from preservative handling, transport, leaks, and valves were not tested.

8.1 TREATING CYLINDER SPILLAGE AND DRIPPAGE

The treating facility tested employed two treating cylinders, and used penta and creosote preservatives. Samples of accumulated spillage and drippage were collected from the area directly beneath the penta and creosote treating cylinder access doors. Two samples were obtained at each location before and after the field test period. Table 8-1 presents the qualitative organic analysis for these samples.

8.2 FUGITIVE EMISSION DURING UNLOADING AND CHARGING OPERATIONS

Air samples were collected during unloading and charging operations directly above the penta and creosote treating cylinder access doors. Sampling was performed using the modified EPA Method 5 train and XAD-2 cartridges described in appendix A.

TABLE 8-1. CHARACTERIZATION OF PENTA AND CREOSOTE TREATING CYLINDER SPILLAGE AND DRIPPAGE

Sample location:	Penta treating cylinder spillage and drippage		Creosote treating cylinder spillage and drippage	
Date collected:	9/23/80	9/25/80	9/23/80	9/25/80
Compound	Concentrations in µg/g			
Pentachlorophenol	1,500	2,100	390	1,800
Phenol	<10	<10	<20	<10
Fluoranthene	29	180	420	200
Naphthalene	50	200	1,300	1,400
Benzo(a)anthracene	60	80	870	1,000
Benzo(a)pyrene	50	5.6	240	200
Benzofluoranthenes	54	26	700	500
Chrysene	50	85	710	850
Acenaphthylene	16	11	72	180
Anthracene	47	55	1,200	1,500
Benzo(ghi)perylene	<10	<5	<50	40
Fluorene	110	140	1,100	2,600
Phenanthrene	150	320	2,300	2,200
Dibenzo(a,h)anthracene	<10	<5	<50	20
Indeno(1,2,3-cd)pyrene	<10	<5	<50	52
Pyrene	24	140	370	1,700
Benzene	<0.5	0.1	0.3	15
Toluene	<0.5	0.5	<0.2	<1
Ethylbenzene	<0.5	0.5	<0.2	<1

Fugitive emissions released through the open cylinder door during charge changes appeared as a dense white plume which persisted throughout the sampling. Table 8-2 presents the qualitative organic analysis for these samples in concentration per volume of air sampled. It was not feasible to quantify a mass emission rate due to large fluctuations in ambient air dilution caused by changing wind speed and direction.

8.3 VACUUM VENT EXHAUST

Certain wood treating processes require the application of pressure and vacuum at various steps of the treating cycle. The pressure release and vacuum exhaust are sources of fugitive emissions, both aerosols and vapors.

Emissions from a vacuum vent common to the penta and creosote treating cylinders were characterized. Grab samples were analyzed onsite for total hydrocarbons (THC) using the procedures described in appendix A. Table 8-3 presents a summary of the results of the THC analysis during both penta and creosote treating cycles.

Grab samples of emissions from the vacuum vent also were analyzed for specific low-molecular-weight hydrocarbons: benzene, toluene, and ethylbenzene. These components were measured onsite using the methods and procedures described in appendix A. Table 8-4 presents a summary of the analyses for specific low-molecular-weight emissions during penta and creosote treating cycles.

These data tables show that significant concentrations of organic compounds are emitted to the atmosphere. During the course of a single treating cycle at this facility, the chronological sequence in table 8-5 was observed.

TABLE 8-2. QUALITATIVE ORGANIC ANALYSIS RESULTS FOR FUGITIVE EMISSIONS

Sample location:	Penta treating cylinder			Creosote treating cylinder
Run number:	1	2	3	1
Compound	Concentration*			
Pentachlorophenol	<0.02	8.12	2.63	0.63
Phenol	<0.02	1.62	<0.02	0.11
Fluoranthene	0.026	<0.16	0.019	0.94
Naphthalene	0.057	5.85	1.86	2.81
Benzo(a)anthracene	<0.02	<0.16	<0.02	0.01
Benzo(a)pyrene	<0.02	<0.16	<0.02	<0.01
Benzofluoranthenes	<0.02	<0.16	<0.02	<0.01
Chrysene	<0.02	<0.16	<0.02	0.01
Acenaphthylene	0.135	0.29	0.11	0.086
Anthracene	0.026	0.05	0.03	0.46
Benzo(ghi)perylene	<0.02	<0.81	<0.02	<0.01
Fluorene	<0.02	0.32	0.46	0.08
Phenanthrene	0.31	0.49	0.28	2.81
Dibenzo(a,h)anthracene	<0.02	<0.81	<0.12	<0.01
Indeno(1,2,3-cd)pyrene	<0.02	<0.16	<0.02	<0.67

*Concentration units are mg/sm^3

TABLE 8-3. SUMMARY OF TOTAL HYDROCARBON DETERMINATIONS PERFORMED AT A COMMON VACUUM VENT

Date	Emission point: Penta pan evaporation device	Creosote pan evaporation device	Penta treating cylinder fugitive emissions	Creosote treating cylinder fugitive emissions	Vacuum vent penta cycle	Vacuum vent creosote cycle
	ppm* total hydrocarbons as methane (time)**					
	evaporation	evaporation	emissions	emissions	penta cycle	creosote cycle
9/23/80	444 (1326)	--	--	--	--	--
9/24/80	--	892 (1730) 36 (1747)	3,660 (1326) 984 (1351) 1,787 (1425)	646 (1519)	--	--
9/25/80	165 (1250) 185 (1305)	1,456 (1450) 1,442 (1514)	--	221 (0828) 365 (0914)	42,066 (1034) 52,294 (1052)	22,117 (1332) 41,475 (1349)

*ppm = parts per million
**(time) = time sample was collected, 24-hr clock

TABLE 8-4. SUMMARY OF SPECIFIC LOW-MOLECULAR-WEIGHT HYDROCARBON DETERMINATIONS AT A COMMON VACUUM VENT

Date	Time (24-hr clock)	Benzene (ppm)	Toluene (ppm)	Ethylbenzene (ppm)	Total hydrocarbon as methane (ppm)
Emission point: penta thermal evaporation device					
9/23/80	1650	1.6	ND	ND	4.6
9/25/80	1250	ND	ND	ND	—
	1305	ND	ND	1.8	6.9
Emission point: creosote thermal evaporation device					
9/24/80	1730	ND	ND	ND	—
	1747	ND	ND	1.5	5.8
9/25/80	1450	ND	ND	13	53
	1514	ND	ND	13	53
Emission point: penta treating cylinder fugitive emissions					
9/24/80	1326	ND	ND	ND	—
	1351	ND	ND	27	110
	1425	ND	ND	11	43
Emission point: creosote treating cylinder fugitive emissions					
9/24/80	1519	ND	ND	ND	—
2/25/80	828	ND	ND	3.3	13
	914	ND	ND	2.1	8.6
Emission point: vacuum vent during penta cycle					
9/25/80	1034	ND	1,567	1,607	11,571
	1052	104	1,482	1,722	12,010
Emission point: vacuum vent during creosote cycle					
9/25/80	1332	1,356	42	1,618	10,106
	1349	1,304	64	1,598	9,960

ND = not detectable

TABLE 8-5. TREATING CYCLE SEQUENCE

Treating Cycle	Pressure or vacuum	Tem. °F	Time started	Time completed	Lapse time (hours)	
CONDITIONING						
1. Steaming						
2. Vacuum	23 in.		8:15 am	10:15 am	2:00	
3. Preservative In.			5:45 am	6:15 am	0:50	
4. Heating in Oil		210	6:15 am	10:15 am	4:00	
5. Preservative Back			10:15 am	10:45 am	0:50	5:00
TREATING						
6. Initial Vacuum						
7. Initial Air	70 psi		10:45 am	11:00 am	0:25	
8. Preservative In.			11:00 am	11:20 am	0:33	
9. Pressure Commenced	90 psi	200	11:20 am	1:30 pm	2:17	
10. Preservative Back		210	1:30 pm	2:00 pm	0:50	
11. Final Vacuum	23 in.		2:00 pm	4:00 pm	2:00	
12. Recovering Drippings			4:00 pm	4:15 pm	0:25	
13. Secondary Steam						
14. Secondary Vacuum						
15. Changing Time						0:50
			TOTAL TIME			11:00

From this table, it can be seen that a vacuum was drawn for a total of 4 hrs, and the retort was open for a total of 50 min. Based on these emission times and the data contained in table 8-3, the vacuum vent represents the greatest emission source. A vacuum vent exhaust of 12.5 sm^3/min with an organic concentration of 50,000 mg/l (50 mg/m^3) results in an emission rate of 625 mg/min. For a plant with two retorts, the annual emission rate would be less than one metric ton/year. A medium refinery may emit as much as 1,000 metric ton/year. Therefore, though these concentrations of organics may cause localized problems, the total emission burden is not significant.